PX262: Quantum Mechanics & its Applications

Finlay Campbell

2021/22

Contents

1 Formalisation of Quantum Mechanics

1.1 Postulates of Quantum Mechanics

Unlike in classical mechanics, the state of a system in quantum mechanics is not defined by the values of dynamical variables. Instead, it is described by a *state function*. The five postulates of quantum mechanics are:

- For every dynamical variable, there exists a state function, from which possible predictions of physical properties of a system can be obtained. Everything that can be known about the system is encapsulated in the state function but the state function itself is not experimentally accessible.
- Observables are dynamical variables of a quantum system accessible to measurement. Each is associated with an *operator*: a mathematical procedure performed on the state function. These must be linear and Hermitian.
- When an operator $\hat{Q}$ acts on a function, the result must be an eigenvalue of $\hat{Q}$. Which eigenvalue is measured is probabilistic rather than deterministic. The probabilities depend on the coefficients c_n of eigenfunctions in the linear superposition of eigenfunctions that represents the quantum state:

  $$\Psi = \sum_n c_n \Psi_n \, . \tag{1.1}$$

  Ψ_n are eigenfunctions of $\hat{Q}$ with respective probabilities $|c_n|^2$.
- The expectation value $\langle q \rangle$ of the observable represented by $\hat{Q}$ is

  $$\langle q \rangle = \int_V \Psi^* \hat{Q} \Psi \, \mathrm{d}\tau \, . \tag{1.2}$$

  This is the mean value of the observable measured over many experiments starting from the same quantum state.
- The time-dependence of the wave function is determined by the time-dependent Schrödinger equation (TDSE):

  $$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \, . \tag{1.3}$$

  Generally, the Hamiltonian is the sum of kinetic and potential energies $\hat{H} = \hat{T} + \hat{V}$.
  If the potential is not time-dependent, we can separate the variables $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) f(t)$ to get the time-independent Schrödinger equation (TISE), solutions to which are called *stationary states*:

  $$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \, . \tag{1.4}$$

  This is an example of an operator eigenvalue equation which, more generally, can be written $\hat{Q}\psi = q\psi$.

1.2 The Correspondence Principle

The *correspondence principle* can be seen as linking quantum and classical mechanics. It states that, in the classical limit, the results of quantum mechanics should agree with those of classical mechanics. This means that, for large quantum numbers, a wavefunction should tend to that of the classically described system. We can also apply the correspondence principle to operators.
Let Ψ be a right-travelling plane wave

$$\Psi = \Psi_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$$

Then

$$\begin{gathered} \boldsymbol{\nabla}\Psi = i\mathbf{k}\Psi \\ -i\hbar\boldsymbol{\nabla}\Psi = \hbar\mathbf{k}\Psi = \mathbf{p}\Psi \end{gathered}$$

Hence, the momentum operator is

$$\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla} \, . \tag{1.5}$$

We can use the correspondence principle to construct new operators. Classically, we know that kinetic energy is given by $T = \frac{p^2}{2m}$. Using eq. 1.5, we get

$$\hat{T} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} = -\frac{\hbar^2}{2m} \nabla^2 \,, \tag{1.6}$$

which must be the kinetic energy operator.

1.3 Hilbert Space & Dirac Notation

A *Hilbert space* is a mathematical framework with which we can describe quantum states as vectors. The basis of these vectors can be freely chosen however it often makes sense to choose the eigenfunctions of a given operator. The eigenfunctions of an operator form a complete Hilbert space with *inner product* defined as

$$\langle \Psi_1 | \Psi_2 \rangle = \int_V \Psi_1^* \Psi_2 \, \mathrm{d}\tau \,. \tag{1.7}$$

The LHS of eq. 1.7 uses Dirac (or bra–ket) notation. $|\Psi\rangle$ is called a "ket" and represents the vector in Hilbert space. $\langle \Psi |$ is called a "bra" and represents the linear mapping of the vector onto the complex plane:

$$\langle \Psi | = |\Psi\rangle^\dagger \,. \tag{1.8}$$

The reversed "ket-bra" $|\phi\rangle\langle\psi|$, or *outer product*, is an operator defined such that $(|\phi\rangle\langle\psi|) \, |a\rangle = |\phi\rangle \, \langle \phi | a \rangle$. One application of this is the *projection operator*: $|\psi\rangle\langle\psi|$; this returns the orthogonal projection of a vector in Hilbert space onto the vector $|\psi\rangle$.
Other properties that are important to remember:

- Basis vectors, or eigenfunctions, are said to be orthonormal if $\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$ is satisfied.
- The inner product in Hilbert space is conjugate symmetric, i.e. $\langle \Psi_i | \Psi_j \rangle = \langle \Psi_j | \Psi_i \rangle^*$.
- Hilbert space consists of the set of square-integrable functions, i.e. $\int_V |\Psi|^2 \, \mathrm{d}\tau$ is finite. In quantum mechanics, these are also normalised.
- The prefactors of eigenfunctions can be written as the inner product $c_n = \langle \psi_n | \psi \rangle$: the overlap between the eigenfunction and the total wavefunction. Subbing this into equation 1.1 gives

$$\begin{aligned} \psi(x) \equiv \int \delta(x - x')\psi(x') \, \mathrm{d}x' &= \int \sum_n \psi_n(x) \psi_n^*(x') \psi(x') \, \mathrm{d}x' \,, \\ \Rightarrow \sum_n \psi_n(x) \psi_n(x') &= \delta(x - x') \,. \end{aligned} \tag{1.9}$$

We can use this notation to express quantum mechanical problems in terms of matrices. The Schrödinger equation can be written as $\hat{H} \, |\psi\rangle = i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \, |\psi\rangle$ and we can choose a complete set of (time-independent) basis vectors $|i\rangle$ such that $|\psi\rangle = \sum_i |i\rangle \, \langle i | \psi \rangle$. Combining these gives

$$\sum_i \hat{H} \, |i\rangle \, \langle i | \psi \rangle = i\hbar \sum_i |i\rangle \, \frac{\mathrm{d}}{\mathrm{d}t} \, \langle i | \psi \rangle \,,$$

which we can project onto basis vector $|j\rangle$:

$$\begin{aligned} \sum_i \langle j | \hat{H} | i \rangle \, \langle i | \psi \rangle &= i\hbar \sum_i \langle j | i \rangle \, \frac{\mathrm{d}}{\mathrm{d}t} \, \langle i | \psi \rangle \,, \\ \sum_i H_{ji} c_i(t) &= i\hbar \frac{\mathrm{d}}{\mathrm{d}t} c_j(t) \,. \end{aligned} \tag{1.10}$$

This is now a matrix equation: c_i and c_j are the components of column vectors and $H_{ji} = \langle j | \hat{H} | i \rangle$ are the components forming a square matrix.

1.4 Operators

1.4.1 Hermitian Operators

As mentioned in section 1.1, operators representing observables must be Hermitian. This means that they equal their Hermitian conjugate $\hat{Q}^\dagger$ which is defined by $\langle f|\hat{Q}^\dagger g\rangle = \langle \hat{Q}f|g\rangle$. Hence,

$$\left\langle f\middle|\hat{Q}g\right\rangle = \left\langle \hat{Q}f\middle|g\right\rangle \, , \tag{1.11}$$

is the hermiticity condition where f, g are valid wavefunctions. The operator complex conjugate is defined as $\hat{Q}^* f^* = (\hat{Q}f)^*$ but, for two operators, $(\hat{A}\hat{B})^* = \hat{B}^*\hat{A}^*$ must be used. An operator can be confirmed to be Hermitian using the definition for its Hermitian conjugate above. For example, consider the momentum operator $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$.

$$\begin{aligned}\langle\phi|\hat{p}_x\psi\rangle &= \int_{-\infty}^{\infty} -\phi^* i\hbar\frac{\partial\psi}{\partial x}\,\mathrm{d}x \\ &= \left[-i\hbar\phi^*\psi\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} -i\hbar\frac{\partial\phi^*}{\partial x}\psi\,\mathrm{d}x\end{aligned}$$

Valid functions are square-integrable and so must vanish to zero as they approach ±∞. This means that the first term equals zero. We are left with

$$\langle\phi|\hat{p}_x|\psi\rangle = \int_{-\infty}^{\infty} i\hbar\frac{\partial\phi^*}{\partial x}\psi\,\mathrm{d}x = \left\langle -i\hbar\frac{\partial\phi}{\partial x}\middle|\psi\right\rangle = \langle\hat{p}_x^\dagger\phi|\psi\rangle$$

Hence, $\hat{p}_x^\dagger = -i\hbar\frac{\partial}{\partial x} = \hat{p}_x$ and so the momentum operator is Hermitian, as expected.
From a generalised eigenvalue equation for operator $\hat{Q}$, it can easily be shown that

$$\begin{aligned}\langle\psi_n|\,\hat{Q}\,|\psi_n\rangle &= \langle\psi_n|q_n\psi_n\rangle \, , \\ &= q_n\,\langle\psi_n|\psi_n\rangle \, .\end{aligned} \tag{1.12}$$

Repeating this with the complex conjugate of said eigenvalue equation yields

$$\langle\psi_n^*|\,\hat{Q}^*\,|\psi_n^*\rangle = q_n^*\,\langle\psi_n^*|\psi_n^*\rangle \, . \tag{1.13}$$

Using the condition in equation 1.11, the LHS of equations 1.12 and 1.13 must be equal. Hence, for normalised wavefunctions,

$$\begin{aligned}q_n\,\langle\psi_n|\psi_n\rangle &= q_n^*\,\langle\psi_n^*|\psi_n^*\rangle \, , \\ q_n &= q_n^* \, .\end{aligned} \tag{1.14}$$

This shows that the eigenvalues of a Hermitian operator must be purely real numbers.
Now, if we multiply the generalised eigenvalue equation by ψ_m^* then integrate, we get

$$\int_V \psi_m^*\hat{Q}\psi_n\,\mathrm{d}\tau = q_n\,\langle\psi_m|\psi_n\rangle \, . \tag{1.15}$$

We can write that the complex conjugate of the eigenvalue equation is $\hat{Q}^*\psi_m^* = q_m\psi_m^*$ now that we know the eigenvalue is real. Multiplying this by ψ_n and integrating gives

$$\int_V \psi_n\hat{Q}^*\psi_m^*\,\mathrm{d}\tau = q_m\,\langle\psi_n^*|\psi_m^*\rangle \, . \tag{1.16}$$

Again, we can use equation 1.11 to show that the LHS of equations 1.15 and 1.16 are equal. Therefore for $n \neq m$, we require

$$\langle\psi_m|\psi_n\rangle = \langle\psi_n^*|\psi_m^*\rangle = 0 \, ,$$

and for $n = m$, we require

$$\langle\psi_n|\psi_n\rangle = 1 \, .$$

Thus, the eigenfunctions of a Hermitian operator form an orthonormal set:

$$\langle\psi_m|\psi_n\rangle = \delta_{mn} \, . \tag{1.17}$$

1.4.2 Expectation Values

Equation 1.2 tells us how to calculate the expectation value of an observable. This applies to both discrete and continuous eigenvalue spectra. This can be shown using equation 1.1.

$$
\begin{aligned}
\langle q \rangle &= \int_V \Psi^* \hat{Q} \Psi \, \mathrm{d}\tau \\
&= \int_V \left(\sum_m c_m \Psi_m \right)^* \hat{Q} \left(\sum_n c_n \Psi_n \right) \mathrm{d}\tau \\
&= \sum_m \sum_n \left(c_m^* c_n \int_V \Psi_m^* \hat{Q} \Psi_n \, \mathrm{d}\tau \right) \\
&= \sum_m \sum_n \left(c_m^* c_n q_n \int_V \Psi_m^* \Psi_n \, \mathrm{d}\tau \right) \\
&= \sum_m \sum_n c_m^* c_n q_n \delta_{mn} \\
&= \sum_n |c_n|^2 q_n
\end{aligned}
$$

This gives an expression for the expectation value as each eigenvalue q_n has a probability $|c_n|^2$ of being measured.[1] Equation 1.2 can also be written as $\langle q \rangle = \langle \Psi | \hat{Q} | \Psi \rangle$ using bra-ket notation. The uncertainty of the expected value is given by the standard deviation σ_q,

$$\sigma_q = \sqrt{\langle q^2 \rangle - \langle q \rangle^2}\,, \tag{1.18}$$

with $\left\langle q^2 \right\rangle = \langle \Psi | \hat{Q}\hat{Q} | \Psi \rangle$.

Time Dependence of Expectation Values

The answer to the question *"Since quantum mechanics abandons local realism, how can a dynamical variable be conserved as it has no precise value?"* is that its expectation value should have no associated time dependence. Consider a Hermitian operator $\hat{Q}$.

$$
\begin{aligned}
\frac{\mathrm{d}\langle q \rangle}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t} \int_V \Psi^* \hat{Q} \Psi \, \mathrm{d}\tau \\
&= \int_V \Psi^* \frac{\partial \hat{Q}}{\partial t} \Psi + \frac{\partial \Psi^*}{\partial t} \hat{Q} \Psi + \Psi^* \hat{Q} \frac{\partial \Psi}{\partial t} \, \mathrm{d}\tau
\end{aligned}
$$

Now, substitute in the time derivative of the wavefunctions from the TDSE (equation 1.3).

$$
\begin{aligned}
\frac{\mathrm{d}\langle q \rangle}{\mathrm{d}t} &= \int_V \Psi^* \frac{\partial \hat{Q}}{\partial t} \Psi - \frac{1}{i\hbar} \left[(\hat{H}^* \Psi^*)(\hat{Q}\Psi) - \Psi^* (\hat{Q}\hat{H}\Psi) \right] \mathrm{d}\tau \\
&= \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle + \frac{i}{\hbar} \int_V \left[\Psi^* \hat{H} \hat{Q} \Psi - \Psi^* \hat{Q} \hat{H} \Psi \right] \mathrm{d}\tau
\end{aligned}
$$

Hence,

$$\frac{\mathrm{d}\langle q \rangle}{\mathrm{d}t} = \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle + \frac{i}{\hbar} \left\langle \left[\hat{H}, \hat{Q} \right] \right\rangle . \tag{1.19}$$

This is Ehrenfest's theorem;[2] it shows that, if a time-independent operator commutes with the Hamiltonian, the expectation value of its associated observable is constant with time, i.e. it is a conserved quantity. We can also use equation 1.19 to determine physical laws. For example, by considering $\hat{Q} = \hat{p}_x$ we recover Newton's 2nd law.

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[1] Note: if you already know the probability of each eigenvalue being measured then it is simpler to just calculate the expectation value directly from this.

[2] More accurately, this is a generalised form of his theorem derived by Werner Heisenberg.

1.4.3 Commutators

The commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}, \tag{1.20}$$

and is not necessarily equal to zero. In the case where the commutator is equal to zero, we say that the two operators *commute* or are *compatible*. The dynamical variables associated with compatible operators can both be known precisely and simultaneously. These eigenvalues must also share a common set of eigenfunctions. It is simple to show that, for example, $[\hat{x}, \hat{p}_x] = i\hbar$ and $[\hat{x}, \hat{p}_y] = 0$. This means that, whilst $\hat{x}$ and $\hat{p}_y$ are compatible, $\hat{x}$ and $\hat{p}_x$ are not. There must therefore exist a minimum uncertainty between the position and momentum of the same coordinate; this is given by Heisenberg's Uncertainty Principle.

The Uncertainty Principle

The Cauchy-Schwarz inequality states that, for two square-integrable functions f and g,

$$\langle f|f\rangle \langle g|g\rangle \geq \left|\langle f|g\rangle\right|^2 . \tag{1.21}$$

The deviation from the expected value of operator $\hat{A}$ is $(\hat{A} - \langle\hat{A}\rangle)$. The expected value of this would clearly be zero but the expected value of its square would not. This means that the root-mean-square deviation σ_a is defined as

$$\begin{aligned} \sigma_a^2 &= \langle\psi|(\hat{A} - \langle A\rangle)^2|\psi\rangle \ , \\ &= \langle\psi|\hat{A}'\hat{A}'|\psi\rangle \ , \\ &= \langle f|f\rangle \ , \end{aligned}$$

where $\hat{A}' = (\hat{A} - \langle\hat{A}\rangle)$ is also a Hermitian operator and f has been defined as $f = \hat{A}'\psi$. Similarly, another operator $\hat{B}$ would have a variance given by $\sigma_b^2 = \langle g|g\rangle$ with $g = \hat{B}'\psi$. Combining this with equation 1.21 yields the inequality

$$\begin{aligned} \sigma_a^2\sigma_b^2 &\geq \left|\langle f|g\rangle\right|^2 , \\ &\geq \left[\frac{1}{2i}(\langle f|g\rangle - \langle g|f\rangle)\right]^2 \ , \end{aligned} \tag{1.22}$$

because, for any complex number $z > \text{Im}\{z\} = \frac{1}{2i}(z - z^*)$. We can let $\langle\hat{A}\rangle = a$ and $\langle\hat{B}\rangle = b$ for simplicity and rewrite $(\langle f|g\rangle - \langle g|f\rangle)$.

$$\begin{aligned} |f\rangle = \hat{A}'\,|\psi\rangle \ \Rightarrow \langle f| &= \left[\hat{A}'\,|\psi\rangle\right]^\dagger = \langle\psi|\,\hat{A}' , \\ \langle f|g\rangle &= \langle\psi|\,\hat{A}'\hat{B}'\,|\psi\rangle \ , \\ &= \left\langle \hat{A}'\hat{B}' \right\rangle \ , \\ &= \left\langle (\hat{A} - a)(\hat{B} - b) \right\rangle \ , \\ &= \left\langle \hat{A}\hat{B} - a\hat{B} - b\hat{A} + ab \right\rangle \ , \\ \langle g|f\rangle &= \left\langle \hat{B}\hat{A} - a\hat{B} - b\hat{A} + ab \right\rangle \ , \\ \langle f|g\rangle - \langle g|f\rangle &= \left\langle \left[\hat{A}, \hat{B}\right] \right\rangle \ . \end{aligned}$$

Hence,

$$\sigma_a^2\sigma_b^2 \geq \left[\frac{1}{2i}\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle\right]^2 \ . \tag{1.23}$$

This is the *generalised uncertainty principle*. By substituting in the commutator $[\hat{x}, \hat{p}_x]$, the Heisenberg uncertainty principle $\sigma_x^2\sigma_{p_x}^2 \geq \frac{\hbar}{2}$ is found.

1.4.4 Angular Momentum Operators

Classically, angular momentum is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ where $\mathbf{r}$ is the position vector and $\mathbf{p}$ is the linear momentum vector. This gives the following equations:

$$\begin{aligned} L_x &= yp_z - zp_y \,, \\ L_y &= zp_x - xp_z \,, \\ L_z &= xp_y - yp_x \,. \end{aligned}$$

These, due to the correspondence principle, can be converted into operator language:

$$\begin{aligned} \hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \,, \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \,, \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \,. \end{aligned} \tag{1.24}$$

The linear momentum operators were defined in section 1.2. We can also define a total momentum operator as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \,. \tag{1.25}$$

We can now consider which combinations of angular momentum operators commute, and which do not. First, $[\hat{L}_x, \hat{L}_y]$:

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) - (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) \\ &= \hat{y}\hat{p}_z\hat{z}\hat{p}_x - \hat{y}\hat{p}_z\hat{x}\hat{p}_z - \hat{z}\hat{p}_y\hat{z}\hat{p}_x + \hat{z}\hat{p}_y\hat{x}\hat{p}_z - \hat{z}\hat{p}_x\hat{y}\hat{p}_z + \hat{z}\hat{p}_x\hat{z}\hat{p}_y + \hat{x}\hat{p}_z\hat{y}\hat{p}_z - \hat{x}\hat{p}_z\hat{z}\hat{p}_y \end{aligned}$$

All terms in the second, third, sixth, and seventh terms commute; thus, the second and seventh and third and sixth terms can be rearranged and cancelled. So we get

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= \hat{y}\hat{p}_z\hat{z}\hat{p}_x + \hat{z}\hat{p}_y\hat{x}\hat{p}_z - \hat{z}\hat{p}_x\hat{y}\hat{p}_z - \hat{x}\hat{p}_z\hat{z}\hat{p}_y \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{x}\hat{p}_z, \hat{z}\hat{p}_y] \\ &= \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x - \hat{x}[\hat{p}_z, \hat{z}]\hat{p}_y \\ &= i\hbar(\hat{y}\hat{p}_x - \hat{x}\hat{p}_y) \\ &= -i\hbar\hat{L}_z \end{aligned}$$

Using the same method for the other components, we get the following set of equations,

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= -i\hbar\hat{L}_z \,, \\ \left[\hat{L}_y, \hat{L}_z\right] &= -i\hbar\hat{L}_x \,, \\ \left[\hat{L}_z, \hat{L}_x\right] &= -i\hbar\hat{L}_y \,. \end{aligned} \tag{1.26}$$

Note how the indices permute.
But, what about the total angular momentum? We can find the commutator of the magnitude of angular momentum with each of the components. First, consider $\hat{L}_x$ which gives

$$\begin{aligned} \left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x\right] &= \left[\hat{L}_x^2, \hat{L}_x\right] + \left[\hat{L}_y^2, \hat{L}_x\right] + \left[\hat{L}_z^2, \hat{L}_x\right] \\ &= \left[\hat{L}_y^2, \hat{L}_x\right] + \left[\hat{L}_z^2, \hat{L}_x\right] \end{aligned}$$

since the commutator of $\hat{L}_x$ with its square equals zero.
We can use the identity that $[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\,\hat{C}$ to get

$$\begin{aligned} \left[\hat{L}^2, \hat{L}_x\right] &= -\hat{L}_y\left[\hat{L}_x, \hat{L}_y\right] - \left[\hat{L}_x, \hat{L}_y\right]\hat{L}_y - \hat{L}_z\left[\hat{L}_x, \hat{L}_z\right] - \left[\hat{L}_x, \hat{L}_z\right]\hat{L}_z \\ &= -i\hbar\hat{L}_y\hat{L}_z - i\hbar\hat{L}_z\hat{L}_y + i\hbar\hat{L}_z\hat{L}_y + i\hbar\hat{L}_y\hat{L}_z \\ &= 0 \end{aligned}$$

The same approach can be used for the other components, yielding the following set of equations

$$\begin{aligned} \left[\hat{L}^2, \hat{L}_x\right] &= 0\,, \\ \left[\hat{L}^2, \hat{L}_y\right] &= 0\,, \\ \left[\hat{L}^2, \hat{L}_z\right] &= 0\,. \end{aligned} \tag{1.27}$$

From this, we can deduce that the both the total angular momentum and *one* of its components are allowed to be known simultaneously; these must share a common set of eigenfunctions. Conventionally, the component of $\mathbf{L}$ that we allow to be known is L_z.

2 Potential Wells

2.1 Particle in a Box

Let there be some one-dimensional region with a constant potential V. The TISE becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = (E - V)\psi\,,$$

which has solutions of the form $\psi = Ae^{ikx}$ so that $E - V = \frac{\hbar^2 k^2}{2m}$.

- For $E - V > 0$, ψ is oscillatory.
- For $E - V < 0$, ψ is an exponential decay.

Consider an infinite potential well of length L with potential $V = 0$ defined inside the well. Since there is an infinite potential outside the well, the wavefunction must have a value of zero here, i.e. there is no probability of the particle existing. Satisfying this boundary condition gives rise to energy eigenvalues:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}\,. \tag{2.1}$$

The states are described by the quantum number $n \in \mathbb{Z}^+$. Note how there is no $E = 0$ state as this would violate the Heisenberg uncertainty principle.
Now, consider the finite potential well where the potential outside the well is V_0. The solutions to the TISE must be continuous and differentiable. For bound states, $E < V_0$ and the wavefunction will be oscillatory inside the well but exponentially decaying outside it. Therefore there will be a non-zero probability of the particle existing in the classically forbidden region outside the well. The energy levels of these states will be quantised; although, the eigenvalue spectrum cannot be solved analytically. Conversely, unbounded states occur for $E > V_0$ and mean that the wavefunction will be oscillatory both inside and outside the well, albeit with different frequencies. This means that there is a continuous energy spectrum above V_0. Both the finite and infinite potential wells are shown in figure 1.
The concepts of the "1D box" can easily be extended to higher dimensions where further quantum numbers would be required to describe a particular state. For example, a particle in a 3D box could be described by $n_x\,, n_y\,, n_z$. A 2D case is depicted in figure 2.

2.2 The Simple Harmonic Oscillator

Many physical situations, e.g. molecular vibrations, can be modelled by quadratic potentials which lead to simple harmonic oscillations. By comparing to the square potential well wavefunctions, we can infer that the ground state solution $u_0(x)$ will look like a Gaussian. By subbing this and a potential of $V = \frac{1}{2}k'x^2$ into the TISE, we find that the energy E_0 is given by[3]

$$E_0 = \frac{\hbar^2}{2}\sqrt{\frac{k'}{m}} = \frac{1}{2}\hbar\omega\,, \tag{2.2}$$

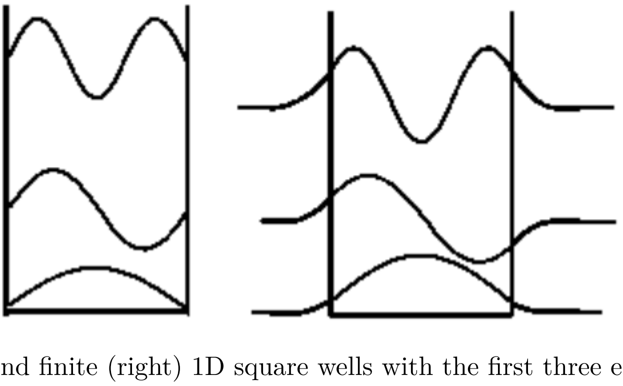

Figure 1: Infinite (left) and finite (right) 1D square wells with the first three eigenfunctions illustrated.

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[3] For the case of diatomic molecular vibrations, the effective spring constant k' gives the strength of the bond and the mass m is really the reduced mass of the system $\mu = \frac{m_1 m_2}{m_1+m_2}$.

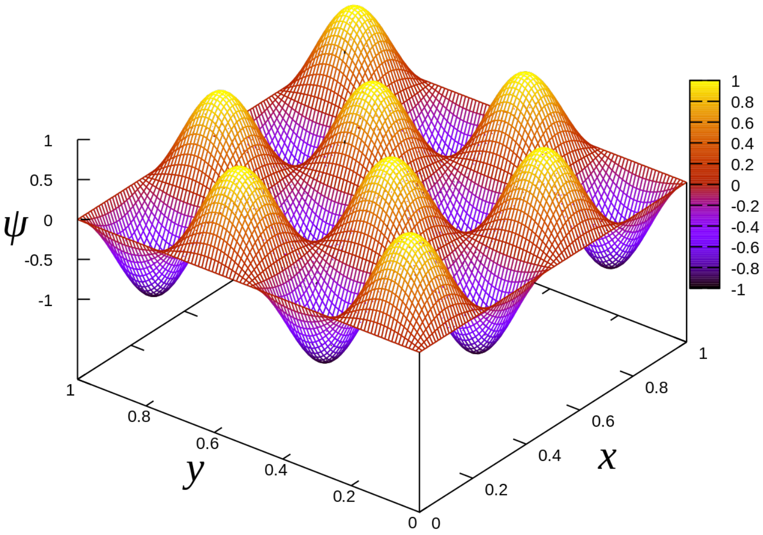

Figure 2: Wavefunction of a particle in a 2D well with $n_x = 4\,, n_y = 4$.

where ω is the classical frequency. We also get that the wavefunction is given by

$$u_0(x) = c_0 \exp\left(-\frac{m\omega x^2}{2\hbar}\right), \tag{2.3}$$

with c_0 being determined by applying the normalisation condition. For higher energy states, it is expected that the symmetry of the wavefunctions will alternate between being even $(u_0, u_2, u_4, ...)$ and odd $(u_1, u_3, u_5, ...)$ and will have an increasing number of extrema. To account for this, we can multiply the wavefunction by an nth degree polynomial. The polynomials which cause the functions to satisfy the Schrödinger equation are called the Hermite polynomials and are outlined in table 1.

n	H_n(x)	Symmetry	E_n
0	1	even	$\frac{1}{2}\hbar\omega$
1	$2x$	odd	$\frac{3}{2}\hbar\omega$
2	$4x^2 - 2$	even	$\frac{5}{2}\hbar\omega$
3	$8x^3 - 12x$	odd	$\frac{7}{2}\hbar\omega$

Table 1: The first four Hermite polynomials $H_n(x)$.

2.2.1 Ladder Operators

A more rigorous approach than “guessing” the form of the wavefunctions is by using ladder operators. These are operators which act on another operator to either raise or lower the quantum number of the eigenvalue. First, we can simplify the problem by working in a unit system where lengths are in units of $(\frac{\hbar}{m\omega})^{\frac{1}{2}}$ and energies are in units of $\hbar\omega$. This results in the dimensionless quantities of *reduced length* $\tilde{x}$ and *reduced energy* $\tilde{E}$.

$$\tilde{x} = \sqrt{\frac{m\omega}{\hbar}}x$$
$$\tilde{E} = \frac{1}{\hbar\omega}E$$

The Hamiltonian operator then becomes:

$$\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 = E \\
\hat{H} &= -\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}\tilde{x}}{\mathrm{d}x}\right)^2 \frac{\mathrm{d}^2}{\mathrm{d}\tilde{x}^2} + \frac{1}{2}m\omega^2\left(\frac{\hbar}{m\omega}\right)\tilde{x}^2 = \hbar\omega\tilde{E} \\
\hat{H} &= \frac{1}{2}\left(\tilde{x}^2 - \frac{\mathrm{d}^2}{\mathrm{d}\tilde{x}^2}\right) = \tilde{E}
\end{aligned}$$

We can define the ladder operators

$$\begin{aligned}
\hat{a}_+ &= \frac{1}{\sqrt{2}}\left(\tilde{x} - \frac{\mathrm{d}}{\mathrm{d}\tilde{x}}\right), \\
\hat{a}_- &= \frac{1}{\sqrt{2}}\left(\tilde{x} + \frac{\mathrm{d}}{\mathrm{d}\tilde{x}}\right),
\end{aligned} \tag{2.4}$$

where $\hat{a}_+$ is the raising operator and $\hat{a}_-$ is the lowering operator. We can find that the commutator of these is $[\hat{a}_+, \hat{a}_-] = -1$ and we can express the Hamiltonian as $\hat{H} = \hat{a}_+\hat{a}_- + \frac{1}{2} = \hat{a}_-\hat{a}_+ - \frac{1}{2}$. Using these, we can show that $\left[\hat{a}_+, \hat{H}\right] = -\hat{a}_+$; we can then apply this to an eigenfunction u_n:

$$\begin{aligned}
\left[\hat{a}_+, \hat{H}\right]u_n &= -\hat{a}_+ u_n \\
\hat{a}_+\hat{H}u_n - \hat{H}\hat{a}_+u_n &= -\hat{a}_+u_n \\
\tilde{E}_n\hat{a}_+u_n - \hat{H}\hat{a}_+u_n &= -\hat{a}_+u_n \\
\tilde{E}_n u_n' - \hat{H}u_n' &= -u_n' \\
\hat{H}u_n' &= (\tilde{E}_n + 1)u_n'
\end{aligned}$$

Here, $u_n' = \hat{a}_+u_n$ is another eigenfunction of the Hamiltonian with an eigenvalue of $\tilde{E}_n + 1$. Similarly, the applying the lowering operator to an eigenfunction will reduce the energy eigenvalue by 1.
Operating on the ground state function with the lowering operator should return zero as, by definition, there is no lower state.

$$\begin{aligned}
\hat{a}_-u_0 &= 0 \\
\hat{a}_+\hat{a}_-u_0 &= 0 \\
\left(\hat{H} - \frac{1}{2}\right)u_0 &= 0 \\
\hat{H}u_0 &= \frac{1}{2}u_0
\end{aligned}$$

This gives us a zero-point energy of the system. Converting back from the reduced unit system gives us the eigenvalue spectrum:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega\,. \tag{2.5}$$

Also by operating on the ground state function with $\hat{a}_-$, the eigenfunctions can be found by solving a simple differential equation.

$$\begin{aligned}
\hat{a}_-u_0 &= 0 \\
\frac{1}{\sqrt{2}}\left(\tilde{x} + \frac{\mathrm{d}}{\mathrm{d}\tilde{x}}\right)u_0 &= 0 \\
\frac{\mathrm{d}u_0}{\mathrm{d}\tilde{x}} &= -\tilde{x}u_0 \\
\frac{\mathrm{d}u_0}{\mathrm{d}x} &= -\frac{m\omega}{\hbar}u_0 \\
\Rightarrow u_0 &= \exp\left(-\frac{m\omega x^2}{2\hbar}\right)
\end{aligned} \tag{2.6}$$

Further eigenfunctions can be found by operating on this with $\hat{a}_+$.

3 Modelling Atoms

3.1 The Hydrogen Atom

We can model the behaviour of electrons in a potential set up by the nucleus of an atom and the other electrons. The simplest case to consider is that of one proton and one electron: a hydrogen atom. Due to the symmetry of the problem, it is easier to consider the position of the electron given by the vector $\mathbf{r}(r,\theta,\phi)$ in spherical polar coordinates. Using the definition of the Laplacian in this coordinate system:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\,, \tag{3.1}$$

we can write the TISE for the electron in a time-independent point-like central potential $V = V(r)$.

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(\mathbf{r})}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(\mathbf{r})}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(\mathbf{r})}{\partial\phi^2}\right] + V(r)\psi(\mathbf{r}) = E\psi(\mathbf{r})\,.$$

We can assume that the wavefunction can be expressed in the form $\psi(\mathbf{r}) = R(r)\Theta(\theta)\Phi(\phi)$ which, once rearranged, gives

$$\frac{\sin^2\theta}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(E - V(r)\right) = -\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}\,.$$

Note, the LHS of is purely a function of r,θ whereas the RHS is a function of ϕ only. The only way that this can be true for all values of r,θ,ϕ is if both sides equal some constant. We can call this m_ℓ^2:

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + m_\ell^2\Phi = 0\,. \tag{3.2}$$

We can now separate the LHS into a function of r and a function of θ.

$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2mr^2}{\hbar^2}\left(E - V(r)\right) = \frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\,.$$

We can set both sides of this equal to the constant $\ell(\ell+1)$:

$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \left[\ell(\ell+1) - \frac{m_\ell^2}{\sin^2\theta}\right]\Theta = 0\,, \tag{3.3}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2mR}{\hbar^2}\left(E - V(r)\right) - \frac{\ell(\ell+1)R}{r^2} = 0\,. \tag{3.4}$$

This technique is called *separation of variables* and has reduced the PDE to three ODEs (equations 3.2, 3.3, 3.4). The first two can be solved for the constants ℓ and m_ℓ but the third depends on the potential function $V(r)$. This means that all central potentials have the same Θ and Φ solutions but the solutions of R require a potential to be specified.
The combined solutions of equations 3.2 and 3.3 form the spherical harmonics Y_{ℓ,m_ℓ}.

$$Y_{\ell,m_\ell}(\theta,\phi) = (-1)^{m_\ell}\left[\frac{2\ell+1}{4\pi}\frac{(\ell-|m_\ell|)!}{(\ell+|m_\ell|)!}\right]^{\frac{1}{2}} P_\ell^{m_\ell}(\cos\theta)e^{im_\ell\phi}\,. \tag{3.5}$$

Where $P_\ell^{m_\ell}(\cos\theta)$ represents a function involving the Legendre polynomials P_ℓ with argument $\cos\theta$. The spherical harmonics quickly become rather complex functions; the first few are depicted in figure 3. For the case of a Coulomb potential set up by a single proton, the radial equation solves to give an eigenvalue spectrum of

$$E_n = -\frac{E_0}{n^2}\,, \tag{3.6}$$

with $E_0 = \frac{me^4}{2\varepsilon_0^2\hbar^2} \approx 13.6\,\mathrm{eV}$ being the Rydberg energy. We now have the three quantum numbers expected from the three spatial degrees of freedom for the electron. These are shown in table 2 along with the final quantum number: the spin quantum number. By operating on the solutions of Y_{ℓ,m_ℓ} with $\hat{L}^2$ and $\hat{L}_z$, two eigenvalue equations can be formed to give the values of the magnitude and z-component of angular momentum. This results in two equations which are true for any central potential:

$$L = \hbar\sqrt{\ell(\ell+1)}\,, \tag{3.7}$$

$$L_z = \hbar m_\ell\,. \tag{3.8}$$

Symbol	Name	Represents	Permitted Values
n	principal	shell	$n \in \mathbb{Z}^+$
ℓ	azimuthal	subshell	$0 \leq \ell < n$
m_ℓ	magnetic	orbital orientation	$-\ell \leq m_\ell \leq \ell$
m_s	spin	electron spin	$-s \leq m_s \leq s$

Table 2: The four quantum numbers which fully describe the state of an electron in a Coulomb potential.

The quantum state of the electron can be labelled by these quantum numbers, or by using spectroscopic notation. This comprises a number corresponding to the n value and a letter: s, p, d, f, g which correspond to $\ell = 0,\ 1,\ 2,\ 3,\ 4$. For example, 3p refers to the $n = 3,\ \ell = 1$ subshell.

3.2 Hydrogen-like Atoms

Hydrogen-like (or hydrogenic) atoms can be defined as an atom with a single valence electron. The obvious examples are the ions with only one electron such as He^+ and Li^{2+}; however, there are other examples including the alkali metals (Li, Na, ...) and singly ionised alkaline earth metals (Be^+, Mg^+, ...). The behaviour of the valence electron can be considered to be the same as that in a hydrogen atom except the positive central charge now comprises multiple protons and potentially core electrons. Because the spherical harmonic solutions do not depend on the specific potential function, only the radial part of the solution will be different to the hydrogen atom solutions. The radial equation (equation 3.4) becomes

$$\left[-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)+\frac{\ell(\ell+1)\hbar^2}{2mr^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]R_{n\ell}(r)=ER_{n\ell}(r)\,, \tag{3.9}$$

which has solutions of

$$R_{n\ell}(r)=C_{n\ell}L_{n\ell}\left(\frac{r}{a_\mathrm{B}}\right)\exp\left(-\frac{Zr}{na_\mathrm{B}}\right). \tag{3.10}$$

Here, e is the elementary charge, $C_{n\ell}$ is a normalisation constant, $L_{n\ell}$ is the generalised Laguerre polynomials with argument $\frac{r}{a_\mathrm{B}}$, and a_B is the Bohr radius. The exponential term crushes the Laguerre polynomials for large radii meaning the electrons are in bound states. These eigenfunctions of give rise to the energy eigenvalue spectrum

$$E_n=-\frac{Z^2E_0}{n^2}\,, \tag{3.11}$$

which clearly reduces to equation 3.6 for the hydrogen atom case of $Z = 1$. These relationships were known empirically decades before the developments of quantum mechanics. This was called the Rydberg formula and was determined through observing the optical spectra of alkali metals.

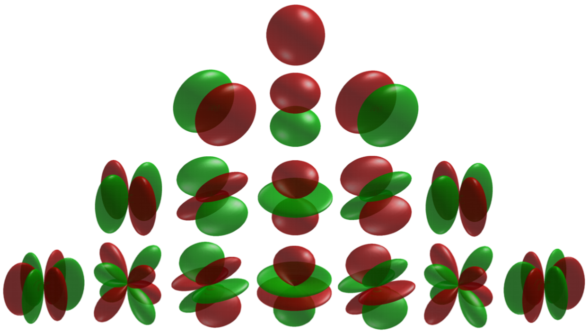

Figure 3: Visual representation of the $\ell = 0$ to $\ell = 3$ spherical harmonics. The m_ℓ values increase from left to right with the azimuthally symmetric $m_\ell = 0$ plots shown in the middle. Red indicates where the function is positive, and green where it is negative. The radial distance of each surface shows the probability as a function of the angular coordinate (θ, ϕ).

3.3 Angular Momentum in Atoms

3.3.1 Orbital Angular Momentum

In section 2.2.1 ladder operators for the case of the simple harmonic oscillator energy states were derived. Using a similar method (but with spherical harmonic eigenvalue functions rather than the TISE), we can show that the ladder operators for the angular momentum in a hydrogen-like atom can be defined as

$$\begin{aligned} \hat{L}_+ &= \hat{L}_x + i\hat{L}_y \,, \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y \,. \end{aligned} \tag{3.12}$$

These operators raise or lower the z-component of angular momentum whilst leaving the total angular momentum unchanged. Instead of just considering the bottom "rung" of the ladder as for the SHO case, both a top and bottom "rung" need to be considered for $\hat{L}_\pm$ in order to obtain the eigenvalue spectrum. We will have a β_{min} and β_{max} where

$$\hat{L}_+ Y_{\alpha,\beta_{\text{max}}} = 0\,; \quad \hat{L}_- Y_{\alpha,\beta_{\text{min}}} = 0$$

This means that

$$\begin{aligned} \hat{L}_-\hat{L}_+ Y_{\alpha,\beta_{\text{max}}} &= 0 \\ (\hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z) Y_{\alpha,\beta_{\text{max}}} &= 0 \\ \hat{L}^2 Y_{\alpha,\beta_{\text{max}}} - \hat{L}_z^2 Y_{\alpha,\beta_{\text{max}}} - \hbar\hat{L}_z Y_{\alpha,\beta_{\text{max}}} &= 0 \\ L^2 Y_{\alpha,\beta_{\text{max}}} - L_{z,\,\text{max}}^2 Y_{\alpha,\beta_{\text{max}}} - \hbar L_{z,\,\text{max}} Y_{\alpha,\beta_{\text{max}}} &= 0 \end{aligned}$$

which has non-trivial solutions of

$$L^2 = L_{z,\,\text{max}}(L_{z,\,\text{max}} + \hbar)\,. \tag{3.13}$$

Similarly for β_{min} we get $L^2 = L_{z,\,\text{min}}(L_{z,\,\text{min}} - \hbar)$. Equating these two equations gives non-trivial solutions of $L_{z,\,\text{max}} = -L_{z,\,\text{min}}$. Because the difference between β_{min} and β_{max} must be an integer multiple of $\hbar$, we get[4]

$$L_{z,\,\text{max}} = \frac{n}{2}\hbar = -L_{z,\,\text{min}}$$

Only even values of n produce valid spatial wavefunctions where $Y_{\alpha,\beta}(\theta, \phi + 2\pi) = Y_{\alpha,\beta}(\theta, \phi)$ is satisfied (see equation 3.5), so we get

$$L_{z,\,\text{max}} = \ell\hbar\,; \quad L_{z,\,\text{min}} = -\ell\hbar$$

where $\ell = \frac{n}{2}$ is the azimuthal quantum number. This means that the intermediate values of L_z are given by the eigenvalue spectrum $L_z = m_\ell\hbar$ with extrema at $\pm\ell$, as shown in table 2. Using equation 3.13, the eigenvalue spectrum for total angular momentum (equation 3.7) can also be obtained.

3.3.2 Spin Angular Momentum

Spin is a property of particles which acts as an intrinsic angular momentum. For charged particles, this results in a magnetic dipole moment $\boldsymbol{\mu}$ which is experimentally measurable. For an electron this is

$$\boldsymbol{\mu}_e = -\frac{eg}{2m_e}\mathbf{S}\,. \tag{3.14}$$

The g-factor is a dimensionless quantity related to the gyromagnetic ratio (ratio of magnetic moment to angular momentum) and is dependent on the particle. For electron spin, $g \approx 2$. The mathematics of the angular momentum associated with spin mirrors that of orbital angular momentum but with one significant difference: spin can take multiple values at a single point in space. Consequently, spin cannot be described by a spatial wavefunction but rather it requires a *spinor*. We can introduce the set of values $\mathbf{S}$, S_z, s, m_s whose eigenvalue functions/spectra are of the same from as those of $\mathbf{L}$, L_z, ℓ, m_ℓ, as spin is also an angular momentum. Unlike for ℓ, however, both integer and half-integer values of s will produce valid solutions. This sets up a distinction between the two types of particles: bosons with integer spin and fermions with half-integer spin. Electrons are fermions with $s = \frac{1}{2}$, and thus $S_z = \pm\frac{\hbar}{2}$. These two

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[4] Here, n simply refers to any positive integer and not the principal quantum number, which is not directly related to the spherical harmonics.

eigenstates of spin along a particular axis are commonly referred to as "spin-up" and "spin-down", a linear combination of which can describe a general spin state χ:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \,, \tag{3.15}$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} ; \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} , \tag{3.16}$$

as the eigenspinors representing spin-up and spin-down, respectively. The operator must be the 2 × 2 matrix with these as its eigenvectors and $\pm\frac{\hbar}{2}$ as its eigenvalues:

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\sigma_z \,, \tag{3.17}$$

where σ_z is one of the *Pauli spin matrices* (the roots of the 2×2 matrix equation $\sigma^2 = I$). The expected commutator relations (see equations 1.26 and 1.27) hold when the other spin operators are written in this form with the remaining Pauli spin matrices

$$\hat{S}_x = \frac{\hbar}{2}\sigma_x \,; \quad \hat{S}_y = \frac{\hbar}{2}\sigma_y \,,$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} . \tag{3.18}$$

These must also have eigenvalues of $\pm\frac{\hbar}{2}$, and have eigenspinors

$$\chi^x_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} ; \quad \chi^x_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} , \tag{3.19}$$

$$\chi^y_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} ; \quad \chi^y_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix} . \tag{3.20}$$

Because the states spin-up $|{\uparrow}\rangle = \chi_+$ and spin-down $|{\downarrow}\rangle = \chi_-$ form a complete set, we can use equation 1.10 to solve the Schrödinger equation for a general state, as given in equation 3.15. If, for example, the H matrix equals $\left(\begin{smallmatrix} E_0 & A \\ A & E_0 \end{smallmatrix}\right)$, we get

$$\begin{pmatrix} E_0 & A \\ A & E_0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = i\hbar\frac{\partial}{\partial t}\begin{pmatrix} a \\ b \end{pmatrix}$$

The two eigenvalues of this matrix are $E_{\mathrm{I}} = E_0 + A$ and $E_{\mathrm{II}} = E_0 - A$, with corresponding eigenvectors $|\mathrm{I}\rangle = \frac{1}{\sqrt{2}}|{\uparrow}\rangle + \frac{1}{\sqrt{2}}|{\downarrow}\rangle$ and $|\mathrm{II}\rangle = \frac{1}{\sqrt{2}}|{\uparrow}\rangle - \frac{1}{\sqrt{2}}|{\downarrow}\rangle$. Rewriting the function in terms of the new basis gives

$$|\chi\rangle = c(t)\,|\mathrm{I}\rangle + d(t)\,|\mathrm{II}\rangle \tag{3.21}$$

Equation 1.10 then becomes:

$$(E_0 + A)c(t) = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}c(t)\,;$$
$$(E_0 - A)d(t) = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}d(t)\,.$$

These solve to get $c(t) = \frac{1}{\sqrt{2}}e^{-i(E_0+A)t/\hbar}$ and $d(t) = \frac{1}{\sqrt{2}}e^{-i(E_0-A)t/\hbar}$. Hence,

$$\begin{aligned} |\chi(t)\rangle &= \frac{1}{2}e^{-i(E_0+A)t/\hbar}(|{\uparrow}\rangle + |{\downarrow}\rangle) + \frac{1}{2}e^{-i(E_0-A)t/\hbar}(|{\uparrow}\rangle - |{\downarrow}\rangle) \\ &= e^{iE_0t/\hbar}\left[\cos\left(\frac{At}{\hbar}\right)|{\uparrow}\rangle - i\sin\left(\frac{At}{\hbar}\right)|{\downarrow}\rangle\right] \end{aligned}$$

So, the probability at time t of the measuring the system as being spin-up is proportional to $\cos^2\left(\frac{At}{\hbar}\right)$, and the probability is proportional to $\sin^2\left(\frac{At}{\hbar}\right)$ for spin-down.

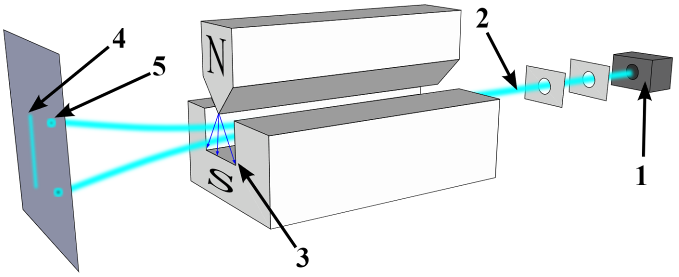


Figure 4: Set-up of the Stern-Gerlach experiment: (1) furnace, (2) beam of silver atoms, (3) inhomogeneous magnetic field, (4) classically expected result, (5) observed result.

Stern-Gerlach Experiment

The Stern-Gerlach experiment, performed in 1922, showed that the orientation of angular momentum is quantised. In this experiment (illustrated in figure 4), a beam of silver atoms is sent through an inhomegeneous magnetic field. This will deflect particles with a non-zero magnetic dipole moment; the force on a magnetic dipole is $\mathbf{F} = \boldsymbol{\nabla}(\boldsymbol{\mu} \cdot \mathbf{B})$. Silver atoms are used as they have one unpaired electron, meaning that their overall spin is $\frac{\hbar}{2}$ along a given axis, but they are also electrically neutral which prevents deflections due to the Lorentz force. The experimental procedure was as follows:

- Silver is heated in a furnace to produce a beam of silver atoms which then pass through a narrow collimating slit.
- The silver atoms are deflected by the magnetic field and are detected on a photographic plate.
- The classically expected result would be a continuous distribution of silver atoms, as each atom could have any orientation of spin.
- However, the beam was split into distinct groups, demonstrating that their spin orientation is quantised.
- This whole experiment has to take place in a vacuum to prevent the scattering of silver atoms.

3.3.3 Spin-Orbit Coupling

The total angular momentum of an electron $\mathbf{J}$ can be written as the sum of orbital and spin components:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \,. \tag{3.22}$$

This can be shown vectorially (see figure 5). Similarly to spin and orbital angular momenta, we can introduce the values J_z, j, m_j. Also, the total magnetic moment can be found by

$$\begin{aligned} \boldsymbol{\mu}_{\text{total}} &= \boldsymbol{\mu}_{\text{orbital}} + \boldsymbol{\mu}_{\text{spin}} \,, \\ &= -\frac{e}{2m_e} \left(\mathbf{L} + 2\mathbf{S} \right) \,. \end{aligned}$$

Unlike with spin, the g-factor of orbital angular momentum is unity, so the total magnetic moment vector is not parallel to the total angular momentum vector. The two types of angular momentum can interact with each other; a classical explanation of why this happens is as follows. From the rest frame of an electron in an $\ell > 0$ state, the nucleus forms a current loop around it, resulting in an effective magnetic field $\mathbf{B}_{\text{eff}}$ due to the orbital angular momentum. The interaction of the spin magnetic moment in this field leads to an energy shift,

$$\Delta E = -\boldsymbol{\mu}_{\text{spin}} \cdot \mathbf{B}_{\text{eff}} \,, \tag{3.23}$$

of the electron's energy state which is called *spin-orbit coupling.* The full quantum treatment of this requires perturbation theory (see PX382/PX3A2) but there are two key results:

- Energy states increase proportional to ℓ and decrease proportional to $\ell + 1$.
- Energy shifts are proportional to the fourth power of the atomic number.

So, although the degeneracy of all $\ell > 0$ spin states is lifted, the effect of this becomes more noticeable for higher ℓ states and, more importantly, for heavier elements. The different states can be labelled by their $j = |l \pm s|$ number, e.g. the 2p state would be split into $2\text{p}_{1/2}$ and $2\text{p}_{3/2}$ levels.

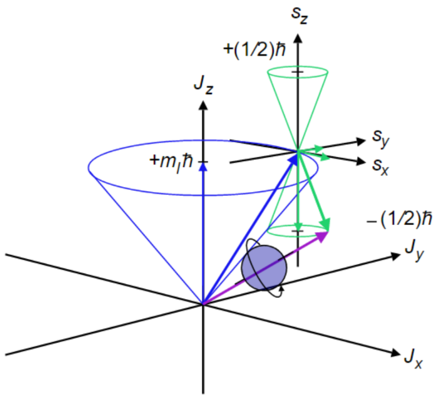


Figure 5: The orbital (blue), spin (green), and total (purple) angular momentum vectors for an electron. The conical shape of the possible vectors reflects the unknown magnitude of the x- and y-components of angular momentum.

3.4 The Zeeman Effect

In the presence of an external magnetic field, the energy states of electrons will be split significantly more than due to spin-orbit coupling. If this magnetic field is applied along the z-axis, it will be the degeneracy of different m_ℓ states which will be lifted. The shifts in energy levels will be given by

$$\begin{aligned}\delta E = \hbar\omega &= -\boldsymbol{\mu}_{\text{orbital}} \cdot \mathbf{B}_{\text{ext}} \\ &= \frac{e}{2m_e} L_z B_{\text{ext}} \quad \text{if } \mathbf{B}_{\text{ext}} = B_{\text{ext}}\hat{\mathbf{z}} \\ &= \frac{e}{2m_e} m_\ell \hbar B_{\text{ext}} \\ &= m_\ell \mu_{\text{B}} B_{\text{ext}}\end{aligned}$$

where $\mu_{\text{B}} = \frac{e\hbar}{2m_e}$ is the Bohr magneton. The allowed optical transitions must follow the selection rules: Because photons have $s = 1$ and angular momentum must be conserved, $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0, \pm 1$. The result of this is that peaks in optical spectra will be split into multiple peaks. The difference between peaks will be

$$\Delta E = \Delta m_\ell \mu_{\text{B}} B_{\text{ext}}\,. \tag{3.24}$$

If ω_0 is the frequency of light emitted in the absence of a magnetic field (or from the $m_\ell = 0$ state which is unaffected by the magnetic field), then three distinct peaks will be seen at ω_0 and $\omega_0 \pm \omega_{\text{L}}$, where $\omega_{\text{L}} = \frac{e}{2m_e} B_{\text{ext}}$ is the Larmor frequency. When spectral lines split into three with the splitting proportional to the applied magnetic field, the effect is called the *normal Zeeman effect*. When a spectrum shows more complicated effects it is called the *anomalous Zeeman effect*. Figure 6 shows an example of the normal Zeeman effect where spin-orbit coupling is also taken into account.

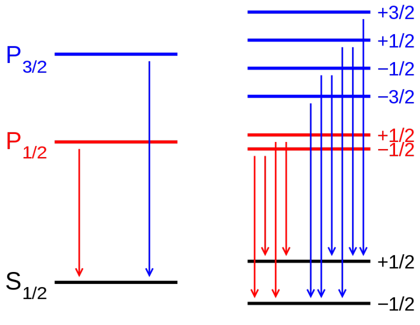


Figure 6: Splitting of optical p-s transitions only considering spin-orbit coupling (left) and with an applied magnetic field causing the Zeeman effect (right). Because spin-orbit coupling is being considered along with the Zeeman effect, it is the m_j states with lifted degeneracy, rather than the m_l states.

3.5 Multielectron Atoms

An important concept in quantum mechanics is that identical particles (e.g. two electrons) cannot be distinguished from one another, even in principle. This means that they must follow *exchange symmetry*: The two electrons can be swapped without changing any physical properties of the system. If we consider a system with two electrons at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, we require

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

for exchange symmetry to be satisfied. The two ways for this to occur are for the wavefunction to be symmetric (bosons) or antisymmetric (fermions) under particle exchange. If the two quantum states of the electrons are denoted by a and b, we can write the combined wavefunction as an antisymmetric combination of the two valid wavefunctions,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\,,$$

which is odd under particle exchange as $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$. If the two electrons were in the same state, i.e. $a = b$, then the wavefunctions would be identically zero and no solution would exist. This is the *Pauli exclusion principle*: No two fermions can exist simultaneously in identical quantum states.

For $n > 1$ electron states, the binding energy is no longer well described by a Coulomb potential. This is because the inner electrons will screen some of the nuclear charge, resulting in a lower attraction to the nucleus. Because this is not a Coulomb potential, the energy eigenvalues of the radial wavefunction will be different. The screened Coulomb potential will tend to $\frac{-Ze^2}{4\pi\varepsilon_0 r}$ close to the nucleus and to $\frac{-e^2}{4\pi\varepsilon_0 r}$ far away from it. This model explains the low ionisation energies of elements with a single valence electron such as lithium which would have an effective nuclear charge of just e; it also explains the high ionisation energies of elements with full valence shells such as neon where the effective nuclear charge is $8e$. Figure 7 shows how ionisation energies vary periodically with Z.

For electrons in the ground state of a multi-electron atom, electrons must "fill up" states from lowest (most negative) to highest energy where two electrons can exist in each n, ℓ, m_ℓ state as there are two values m_s can take. Using spectroscopic notation, superscript can be used (e.g. $1s^2$) to indicate the number of electrons in a particular subshell. Due to spin-spin coupling, the lowest energy states of part-filled subshells will be when the spins are aligned. So the 2p subshell of carbon is [↑↑], and for oxygen it is [↑↓↑↑]. This is Hund's first rule which arises because a symmetric spin wavefunction requires an antisymmetric spatial wavefunction (as the total wavefunction must be antisymmetric for fermions). This forces the electrons further apart, reducing the electrostatic repulsion between them and reducing the screening of the nucleus they experience from one another. Another consequence of the spin-spin interaction is that subshells of similar energies may not be filled in the same order for different atoms. For example, the 4s and 3d subshells of chromium are [↑][↑↑↑↑↑] rather than [↑↓][↑↑↑↑] because the alignment of spins across both subshells results in a lower energy. Also, the binding energies of subshells varies for

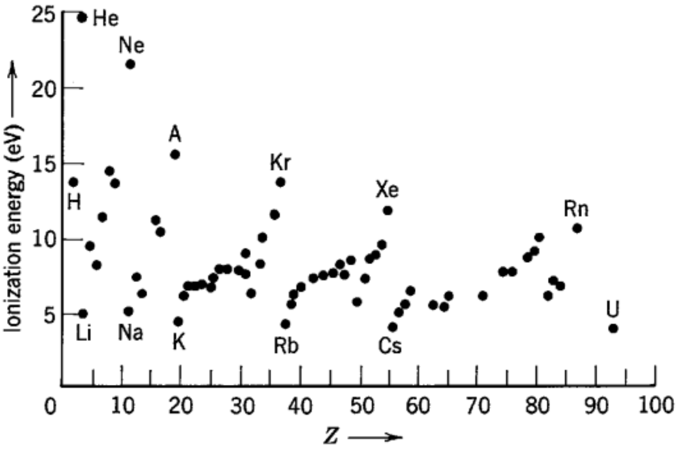


Figure 7: How the first ionisation energy varies with Z. The alkali metals (lowest ionisation energies) and noble gases (highest ionisation energies) have been labelled.

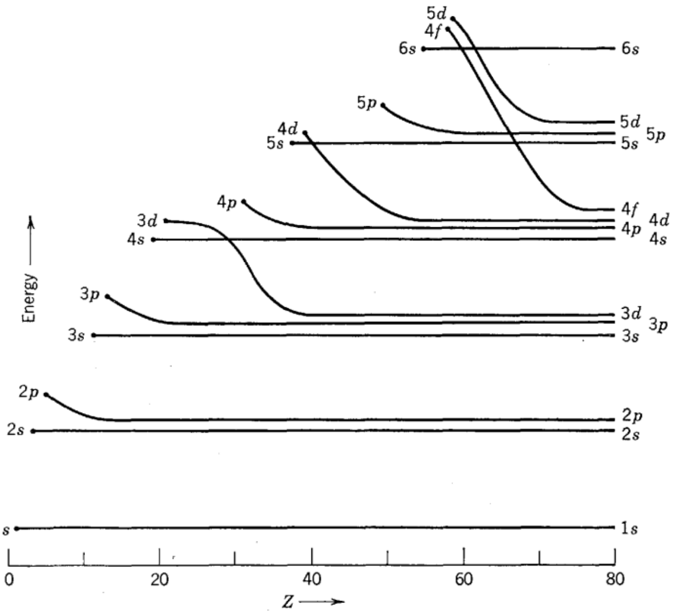


Figure 8: How subshell binding energies vary with Z. For low Z values, the energies are determined by both n and ℓ. For high Z values, the n-dependence dominates the ℓ-dependence of energy.

different elements. This is because, for example, as more 3d electrons are filled, the 4s electrons become more screened from the nucleus. This can be seen in figure 8 and is the reason why the 4s electrons in transition metals have lower ionisation energies than 3d electrons, despite the 3d electrons normally being "filled" last. An explicit example of this are the 4s and 3d subshells of copper: [↑][↑↓↑↓↑↓↑↓↑↓]; the binding energy of the final 3d state is lower than the final 4s state because of the additional nine electrons screening the 4s electrons. Note how, in fig 8, copper ($Z = 29$) is the point where the 3d and 4s lines cross over.

Modelling Multielectron Systems

Consider a He atom where the ith electron has position and spin denoted by $(\mathbf{r}_i, \sigma_i)$. The approximate ground state solution ϕ is

$$\phi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) \approx \phi_\uparrow(\mathbf{r}_1)\phi_\downarrow(\mathbf{r}_2) - \phi_\downarrow(\mathbf{r}_1)\phi_\uparrow(\mathbf{r}_2)\,.$$

The best solutions for $\phi_{\uparrow\downarrow}$ are the solutions to the single-particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{4\pi\varepsilon_0 r} + e\int \frac{\rho_\downarrow(\mathbf{r}')}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'\right]\phi_\uparrow = E_\uparrow\phi_\uparrow(\mathbf{r})\,,$$

where there is an effective potential due to screening containing the charge density $\rho_{\downarrow\uparrow}(\mathbf{r})$ which is set up by the other electron:

$$\rho_\downarrow(\mathbf{r}) = e\phi_\downarrow^*(\mathbf{r})\phi_\downarrow(\mathbf{r})\,.$$

Using numerical methods, these equations can be solved self-consistently, i.e. solving for $\phi_\uparrow$ gives a $\rho_\uparrow$ distribution which can be used to find a better $\phi_\downarrow$ solution (and so on...).

More generally, a many-electron system can be modelled as a single electron moving in a potential set up by nuclei and all the other electrons. Density functional theory (DFT) looks at the electronic density

$$n(\mathbf{r}) = \phi^*(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2 = \mathbf{r}, \ldots)\phi(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2 = \mathbf{r}, \ldots)\,,$$

which is the probability of finding an electron at $\mathbf{r}$. This can be used to find self-consistent solutions to the Schrödinger equation and can be calculated for different nuclear configurations to determine the lowest energy state for the system.

3.6 Molecules

We can expand this model to examine the behaviour of molecules. The Born-Oppenheimer approximation states that, because nuclei move so much slower than electrons, their wavefunctions can be treated separately. We can therefore treat electrons as moving in a static nuclear potential whilst interacting with other electrons. Electrons bond the nuclei of a molecule together in two main ways: covalent and ionic.

Covalent bonding example: H_2
Consider two protons fixed at positions $\mathbf{R}_A$ and $\mathbf{R}_B$ with electrons at positions $\mathbf{r}_1$ and $\mathbf{r}_2$. The Hamiltonian comprises kinetic energy of electrons, electrostatic repulsion of nucleus/nucleus and electron/electron pairs, and electrostatic attraction of electron/nucleus pairs:

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\mathbf{R}_A-\mathbf{R}_B|}+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right)\\ &-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\mathbf{r}_1-\mathbf{R}_A|}+\frac{1}{|\mathbf{r}_2-\mathbf{R}_B|}+\frac{1}{|\mathbf{r}_1-\mathbf{R}_B|}+\frac{1}{|\mathbf{r}_2-\mathbf{R}_A|}\right).\end{aligned}$$

The subsequent Schrödinger equation has an approximate ground state solution of

$$\Psi(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2) = c\,(\mathbf{R}_A-\mathbf{R}_B)\left(\Psi_{100}^A(\mathbf{r}_1)\Psi_{100}^B(\mathbf{r}_2)+\Psi_{100}^B(\mathbf{r}_1)\Psi_{100}^A(\mathbf{r}_2)\right)\times(\uparrow\downarrow),$$

where c is a coefficient depending on the distance between the nuclei, $\Psi_{n\ell m_\ell}$ is the single hydrogen atom solution, and $(\uparrow\downarrow)$ is the combined antiparallel spin state. This means that the system is described as the superposition of electrons being bound to both nuclei and so the electron density is most concentrated between the two nuclei. Hence, the nuclei can be said to be "sharing" the electrons. The energy of this state (see figure 9) is minimised when the internuclear spacing is $R = 0.74$ Å, the bond length of H_2.

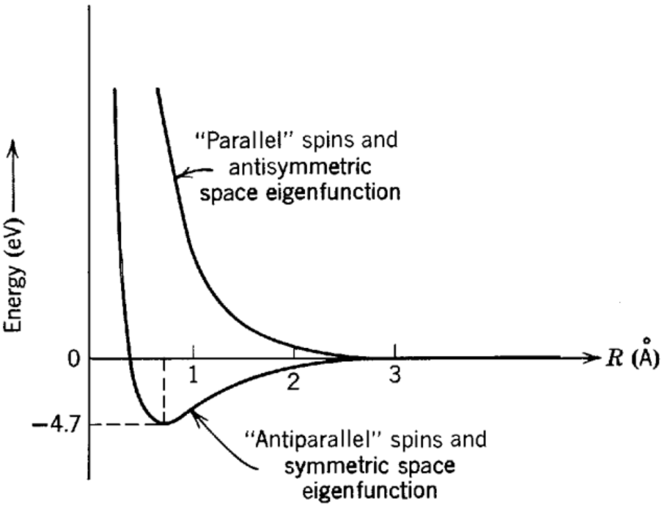


Figure 9: The total energy $E(H_2) - 2E(H)$ of the molecular orbitals as a function of the internuclear separation. The molecule bonds in the state where the electron spins are antiparallel; the state with parallel electron spins is called the antibonding orbital.

Ionic bonding example: NaCl
Sodium has a single valence electron ($3s^1$) and chlorine has seven electrons out of a possible eight in its valence shell ($3s^2\ 3p^5$). The NaCl molecule is well described by the single sodium 3s electron transferring to the 3p shell of chlorine so that they both have full shells. This can occur because sodium has a low ionisation energy and chlorine has a high electron affinity, so the energy required to form two distinct ions (1.3 eV) is lower than the Coulomb potential energy between the two ions (4.9 eV at the equilibrium separation of 2.4 Å). This is shown in more detail in figure 10.

The bonding in a H_2 molecule cannot be described as ionic because the energy required to form the H^+ and H^- ions is greater than the potential energy for all internuclear separations. There are some molecules, such as GaAs, which exhibit behaviour of both types of bonding. Ga ([Ar] $3d^{10}$ $4s^2$ $4p^1$) and As ([Ar] $3d^{10}$ $4s^2$ $4p^3$) can bond covalently in a similar manner to pure Ge ([Ar] $3d^{10}$ $4s^2$ $4p^2$); they can also bond ionically by forming Ga^{3+} and As^{3-} ions, although the latter is slightly less prevalent. Covalent and ionic bonds can be thought of as the two extremes on a continuous spectrum of molecular bonding polarities which are determined by the difference in electronegativities of the two atoms in question.

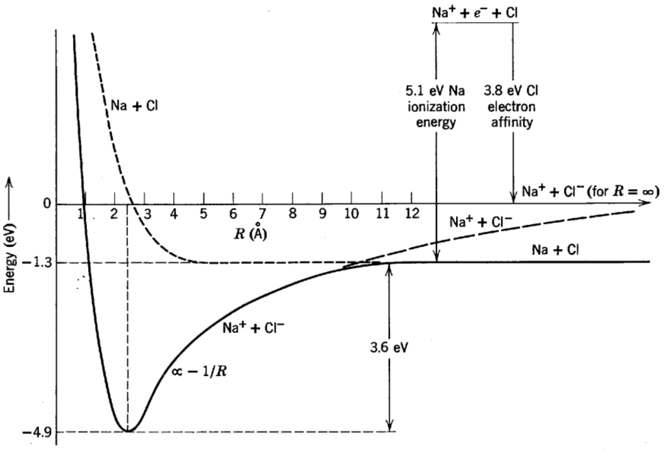


Figure 10: The energy for the neutral atoms Na and Cl, and for the ions Na^+ and Cl^- as functions of the internuclear separation. The ionic combination has lower energy at small separation, while the neutral atomic combination has lower energy at large separation. Thus, as the two neutral atoms are brought together, they form ions once their separation becomes less than a certain value.

3.7 Spectroscopy

Moseley's Law

Moseley's law is an empirical relationship between the characteristic x-ray emission energies and an element's atomic number. It was found that the square root of the x-ray frequency ν has a linear relationship to an effective atomic number Z_{eff}.

Consider an atom which has had a K-shell ($n = 1$) electron knocked out so that a higher-energy electron falls down into its place, emitting a photon. Because the nuclear charge is screened by the remaining K-shell electron, the higher shells have energies proportional to $(Z-1)^2$, rather than Z^2 as for H-atom energy states. Using the Bohr model, we get a characteristic K_α energy of

$$\begin{aligned} E_{\text{K}_\alpha} &= 13.6(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right), \\ \Rightarrow \nu_{\text{K}_\alpha} &\propto (Z-1)^2 . \end{aligned}$$

Moseley also found that $Z_{\text{eff}} = Z - 7.4$ worked well for the L-series (transitions to $n = 2$ states).

XPS

The principle behind x-ray photoelectron spectroscopy (XPS) is that, for an ejected electron, we can infer its binding energy by measuring its kinetic energy. XPS works by irradiating the surface of a material with monochromatic x-rays of frequency ν and measuring the kinetic energies E_k of the ejected electrons. The fundamental equation governing XPS is

$$E_k = h\nu - E_B - \phi\,, \tag{3.25}$$

where E_B is an electron's binding energy, and ϕ is the material's work function. The binding energy is the energy required to remove the electron from an atom; the work function is the further energy required to liberate the free electron from the surface of the material.

Some important features of XPS spectra:

- **Chemical shifts:** The binding energy of electrons is affected by the compound the atom is in. For example, the carbon 1s energy level in a C−O bond is lowered because oxygen is more electronegative than carbon.
- **Staircase background:** The background is due to photoelectrons which have first scattered inelastically rather than being detected directly. After each peak in the spectrum, the background level increases due to these scattered photoelectrons, leading to the staircase effect.
- **Spin-orbit coupling:** This effect can be seen if it is greater than the energy resolution (≈ 1 eV).

Because electrons originating > 1 nm below the surface of a material are very likely to be scattered in the material, their photoelectrons do not produce sharp peaks. This is why XPS is only a useful experimental tool for examining properties and the composition of the *surface* of materials.

4 Modelling Solids

4.1 The Free Electron Model

We can treat valence electrons in a metal as a Fermi gas moving in a uniform potential set by the nuclei and core electrons. For the 1D case, we know from section 2.1 that this gives energy states E_n of

$$E_n = \frac{\hbar^2 k_n^2}{2m} \,. \tag{4.1}$$

The *Fermi number* n_F is the number of occupied states in the ground state of the system and the *Fermi wavenumber* k_F is the wavenumber at that state. For a system with N electrons and length L, $N = 2n_\mathrm{F}$ because there can be two electrons per state, and $k_\mathrm{F} = \frac{n_\mathrm{F}\pi}{L}$. Thus,

$$k_\mathrm{F} = \frac{N\pi}{2L} = \frac{\pi\rho}{2} \,, \tag{4.2}$$

$$E_\mathrm{F} = \frac{\hbar^2\pi^2\rho^2}{8m} \,, \tag{4.3}$$

where E_F is the *Fermi energy* and ρ is the electron density. To model an electron far away from a boundary we need a travelling wave solution and can set up a periodic boundary condition with a period of length L.

$$\phi = Ae^{ikx} = Ae^{ik(x+L)} = \dots$$

This means that $e^{ikL} = 1$ so $k_n = \frac{2n\pi}{L}$. Because positive and negative wavenumbers give different results for a travelling wave, we now have $N = 4n_\mathrm{F}$. Note, equations 4.2 and 4.3 are still true. For $E_n \leq E_\mathrm{F}$,

$$N(E_n) = 4n = \frac{2L}{\pi} k_n = \frac{2L}{\pi} \left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \sqrt{E_n} \,. \tag{4.4}$$

$N(E_n)$ is the total number of electrons with $E \leq E_n$. This distribution becomes a continuum for $L \to \infty$. The *density of states* $n(E)$ can be defined as the number of electrons with energy E and is therefore given by $n(E) = \frac{\mathrm{d}N}{\mathrm{d}E}$ for a continuum of states. From equation 4.4, we therefore get

$$n(E) = \frac{L}{\pi} \left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \frac{1}{\sqrt{E}} \,. \tag{4.5}$$

This means that the total number of electrons can be written $N = \displaystyle\int_0^{E_\mathrm{F}} n(E)\mathrm{d}E$ and the total energy of the system is

$$\begin{aligned} E_\mathrm{tot} &= \int_0^{E_\mathrm{F}} En(E)\mathrm{d}E \,, \\ &= \frac{2L}{3\pi} \left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} E_\mathrm{F}^{\frac{3}{2}} \,. \end{aligned}$$

This means the average energy per electron is $\frac{1}{3}E_\mathrm{F}$.

This can be extended to 3D box with sides of lengths L_x, L_y, L_z. Now, The periodic boundary condition now becomes $e^{ik_xL_x} = e^{ik_yL_y} = e^{ik_zL_z} = 1$ which leads to

$$k_x = \frac{2n_x\pi}{L_x} \,, \quad k_y = \frac{2n_y\pi}{L_y} \,, \quad k_z = \frac{2n_z\pi}{L_z} \,.$$

In the ground state of the system, the filled states will form a sphere in k-space with radius of k_F. This is called the *Fermi surface*. Each state has a volume of $\frac{(2\pi)^3}{L_xL_yL_z} = \frac{8\pi^3}{V}$ where V is the volume of the box. The total number of electrons is then

$$N = \frac{2 \times \frac{4\pi}{3}k_\mathrm{F}^3}{8\pi^3/V} = \frac{Vk_\mathrm{F}^3}{3\pi^2} \,. \tag{4.6}$$

Or $k_\mathrm{F}^3 = 3\pi^2\rho$, which gives a Fermi energy of $E_\mathrm{F} = \frac{\hbar^2}{2m}(3\pi^2\rho)^{\frac{2}{3}}$.

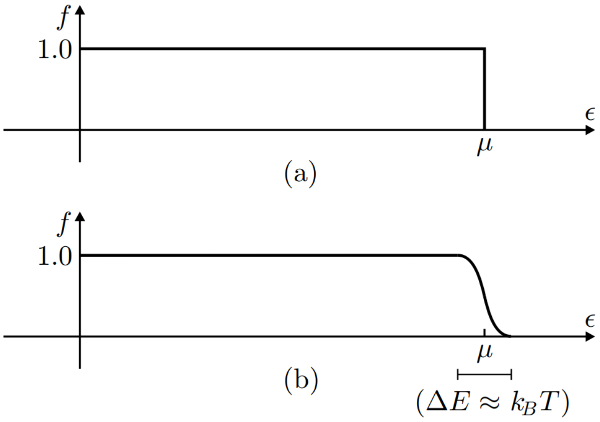


Figure 11: The Fermi-Dirac function for (a) $T = 0$ and (b) finite temperature $T \ll \frac{E_\mathrm{F}}{k_\mathrm{B}}$ shows the average occupancy of each state.

Again, by taking the limit $V \to \infty$, the wavevector values become continuously distributed. The number of electrons below an energy $E \leq E_\mathrm{F}$ are

$$N(E) = \frac{Vk^3}{3\pi^2} = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}}, \tag{4.7}$$

with a density of states

$$n(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}\,.$$

Like for the 1D case, we can calculate the total energy:

$$\begin{aligned} E_\mathrm{tot} &= \int_0^{E_\mathrm{F}} En(E)\mathrm{d}E\,, \\ &= \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_\mathrm{F}^{\frac{5}{2}}\,. \end{aligned}$$

The average energy per electron is then $\frac{3}{5}E_\mathrm{F}$. At temperature $T = 0\,\mathrm{K}$, all states $E \leq E_\mathrm{F}$ are filled and any others are not. For $T > 0\,\mathrm{K}$, this is replaced by the Fermi-Dirac distribution (shown in figure 11).

4.2 Properties of Metals

Heat Capacity

The number of electrons per unit volume which are thermally excited is proportional to $k_\mathrm{B}Tn(E_\mathrm{F})$. These electrons are each excited by approximately $k_\mathrm{B}T$ meaning that the total energy change is given by

$$E_\mathrm{tot} = E_\mathrm{tot}(T = 0) + aT^2\,,$$

for some constant a. Therefore the specific heat at constant volume is given by

$$c_v = \frac{\mathrm{d}E_\mathrm{tot}}{\mathrm{d}T} \propto T\,.$$

This linear dependence is characteristic of metals.

Magnetic Susceptibility

An applied magnetic field will affect spin-up electrons differently to spin-down electrons. An additional term of $-B\hat{\mu}_s$ is added to the Hamiltonian which splits the energies of the states according to their spin state:

$$E = \frac{\hbar^2k^2}{2m} \pm \frac{Beg\hbar}{4m} = \frac{\hbar^2k^2}{2m} \pm \mu_\mathrm{B}B$$

The spin-down states now have a lower energy and so comprise more of the filled states. This means that there is now a net spin and thus an overall magnetisation of

$$M = \mu_{\mathrm{B}}(N_{\downarrow} - N_{\uparrow}) \approx \mu_{\mathrm{B}}^2 B n(E_{\mathrm{F}})$$

So the susceptibility is

$$\chi = \frac{\mathrm{d}M}{\mathrm{d}B} = \mu_{\mathrm{B}}^2 n(E_{\mathrm{F}})$$

$\chi \propto n(E_{\mathrm{F}})$ is another characteristic of metals.

Electrical Conduction

By multiplying the TDSE by Ψ and taking its complex conjugate, we get the two equations

$$\begin{aligned} i\hbar\Psi^*\frac{\partial\Psi}{\partial t} &= -\frac{\hbar^2}{2m}\Psi^*\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi^*\Psi \\ -i\hbar\Psi\frac{\partial\Psi^*}{\partial t} &= -\frac{\hbar^2}{2m}\Psi\frac{\partial^2\Psi^*}{\partial x^2} + V(x)\Psi\Psi^* \end{aligned}$$

Subtracting one from the other gives

$$\begin{aligned} i\hbar\left(\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}\right) &= -\frac{\hbar^2}{2m}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \Psi\frac{\partial^2\Psi^*}{\partial x^2}\right) \\ i\hbar\frac{\partial}{\partial t}(\Psi^*\Psi) &= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right) \end{aligned}$$

This is in the form of the continuity equation: $\boldsymbol{\nabla}\cdot\mathbf{j} = -\frac{\partial\rho}{\partial t}$ because $\Psi^*\Psi$ is the electron density. In 3D, the current density j becomes the current density vector

$$\mathbf{j} = \frac{\hbar}{2im}\left(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\right). \tag{4.8}$$

For a plane wave solution $\Psi = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$, we get

$$\begin{aligned} \mathbf{j} &= \frac{\hbar}{2im}\left(e^{-i\mathbf{k}\cdot\mathbf{r}}i\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} - e^{i\mathbf{k}\cdot\mathbf{r}}(-i\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}\right) \\ &= \frac{\hbar\mathbf{k}}{m}AA^* \end{aligned}$$

This is just the velocity multiplied by the electron density.

4.3 Crystals & Lattices

The free electron model can be made more realistic by considering a lattice arrangement of the nuclei. A crystal is formed when each point in the lattice is occupied by the same *basis*, which can be one or more atoms. A 3D lattice can be thought of as having points described by the vector $\mathbf{R}$ where

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}, \tag{4.9}$$

where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are called the *primitive vectors* and n_1, n_2, $n_3 \in \mathbb{Z}$. The unit cell of the lattice will be a parallelepiped with a volume given by the scalar triple product $V_c = |\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})|$. There are 14 distinct crystal structures in three dimensions, called the Bravais lattices.

The *Wigner-Seitz cell* is the cell constructed around a lattice point from the planes that perpendicularly bisect the vectors connecting the point to its nearest neighbours. Examples of this are shown in figure 12. Repeating the Wigner-Seitz cell fully describes a lattice.

Due to the periodicity of a crystal, we expect properties of the crystal (e.g. electric potential, electron density) to also be periodic. This means some function of position can be expressed as a Fourier series

$$f(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

with $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ as the periodicity condition.

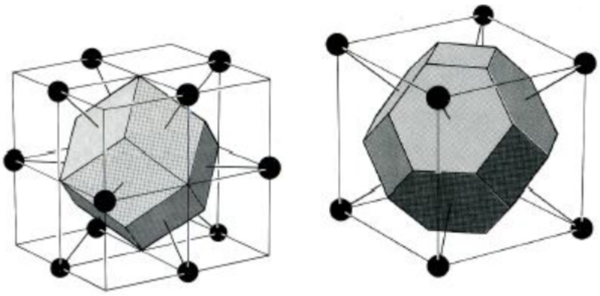


Figure 12: Wigner-Seitz cell for an fcc lattice (left) and a bcc lattice (right).

In the 1D case where we have a lattice with points separated by a, we get that $G_n = \frac{2\pi n}{a}$ in order to satisfy the periodicity with length a. G_n forms another 1D lattice with points separated by $\frac{2\pi}{a}$; hence, this is called *reciprocal space.* For a 3D lattice, each point must be described by three integers h, k, l. We get

$$\mathbf{G}_{hkl} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}\,. \tag{4.10}$$

with the basis vectors in the same direction as in real space but with different magnitudes:

$$\mathbf{A} = \frac{2\pi(\mathbf{b}\times\mathbf{c})}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})} \quad \mathbf{B} = \frac{2\pi(\mathbf{c}\times\mathbf{a})}{\mathbf{b}\cdot(\mathbf{c}\times\mathbf{a})} \quad \mathbf{C} = \frac{2\pi(\mathbf{a}\times\mathbf{b})}{\mathbf{c}\cdot(\mathbf{a}\times\mathbf{b})} \tag{4.11}$$

It is easy to show that $\mathbf{a}_i \cdot \mathbf{A}_j = 2\pi\delta_{ij}$ where $\mathbf{a}_i$ and $\mathbf{A}_j$ just represent one of the basis vectors in real and reciprocal space, respectively. Consider a simple cubic lattice with separation a. This will have $\mathbf{R}_{n_1n_2n_3} = n_1a\hat{\mathbf{i}} + n_2a\hat{\mathbf{j}} + n_3a\hat{\mathbf{k}}$. The reciprocal bases can then be found to be

$$\mathbf{A} = \frac{2\pi}{a}\hat{\mathbf{i}} \quad \mathbf{B} = \frac{2\pi}{a}\hat{\mathbf{j}} \quad \mathbf{C} = \frac{2\pi}{a}\hat{\mathbf{k}}$$

This also forms a simple cubic lattice but now with separation $\frac{2\pi}{a}$. Each value of $\mathbf{G}_{hkl}$ defines a plane in the lattice to which it is perpendicular, e.g. $\mathbf{G}_{001}$ defines the x–y plane.

We can express the potential as a Fourier series as well:

$$V(\mathbf{r}) = \sum_h\sum_k\sum_l V_{hkl}e^{i\mathbf{G}_{hkl}\cdot\mathbf{r}}$$
$$V(\mathbf{r}+\mathbf{R}) = \sum_h\sum_k\sum_l V_{hkl}e^{i\mathbf{G}_{hkl}\cdot(\mathbf{r}+\mathbf{R})} = V(\mathbf{r})$$

The thermal energy of a crystal gives rise to phonons (quantised lattice vibrations). These distort the potential function and cause it to be time-dependent. This is the cause of electron scattering and electrical resistance of materials.

The Wigner-Seitz cell in reciprocal space is called the *Brillouin zone.* The wavevector $\mathbf{k}$ also lies in reciprocal space as it is related to the reciprocal of wavelength (which is related to the spacing a). The values of wavevector that lie in the first Brillouin zone of the 1D reciprocal lattice are $-\frac{\pi}{a} < k < \frac{\pi}{a}$. This sets up the so-called nearly free electron model where the Hamiltonian of an electron is that of a free electron perturbed by a periodic weak potential due to positive charges. In a system of well separated atoms, the allowed electron energy states are set by those of a single atom. If these atoms are moved closer together, the wavefunctions distort and overlap with each other, "smearing" the allowed energies. An electron moving through a crystal has a certain probability of being reflected each time it approaches a positive charge. Normally, the reflected wave will have a negligible effect on the system but, if the electron has a wavelength of $\frac{n\pi}{a}$, the reflected wave will be perfectly out of phase with the incoming wave and the electron will not be able to travel through the crystal. This results in energy gaps at the Brillouin zone boundaries; this is illustrated in figure 13. Unlike in the free electron model, the energy of electrons in k-space is aniostropic in the nearly free model (as shown in figure 14).

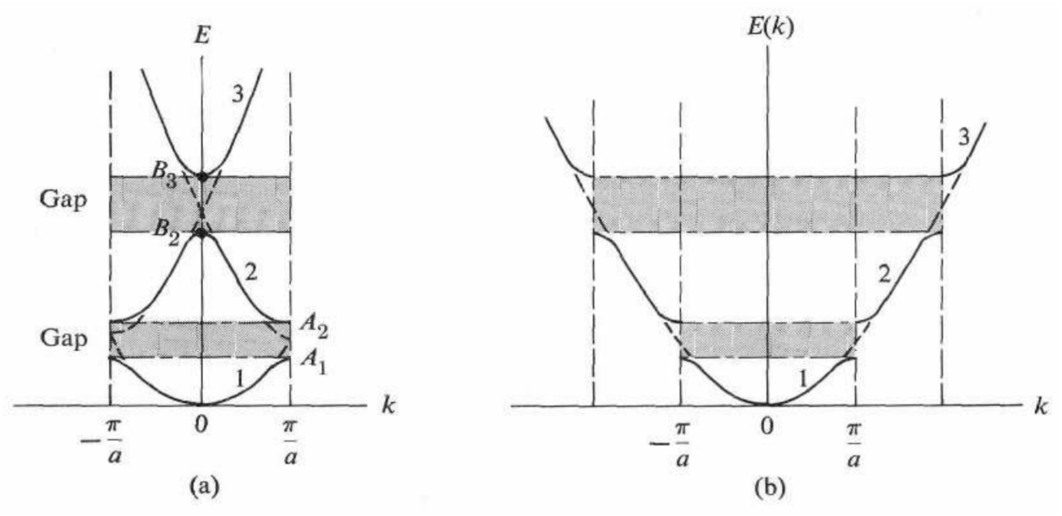


Figure 13: Dispersion curves in the nearly free electron model in (a) the reduced-zone scheme which can be plotted due to the periodicity of the lattice; (b) the extended-zone scheme. There are gaps at the Brillouin zone boundaries unlike the $E \propto k^2$ from the free electron model.

Kronig-Penney Model

Consider a periodic array of square potential barriers of width b and separation a. Bloch's theorem states that the electronic wavefunction must be of the form

$$\psi_k(x) = e^{ikx}u(x)\,, \tag{4.12}$$

where $u(x) = u(x+a) = u(x+2a) = \ldots$ to ensure that the probability distribution is periodic:

$$\psi_k(x+a) = e^{ika}\psi_k(x)\,.$$

Therefore we only need to find a (smooth and continuous) solution for $0 < x < a$, and we have a solution across any domain. We can directly solve the Schrödinger equation within this region. For $0 < x < a - b$ (where $V = 0$) we have $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi_{\mathrm{I}}(x) = E\Psi_{\mathrm{I}}(x)$:

$$\Psi_{\mathrm{I}}(x) = Ae^{i\alpha x} + Be^{-i\alpha x} \quad \text{with } \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$
$$\Psi_{\mathrm{I}}(x) = e^{ikx}\left(Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x}\right)$$

For $a - b < x < a$ (where $V = V_0$) we have $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi_{\mathrm{II}}(x) + V_0\Psi_{\mathrm{II}}(x) = E\Psi_{\mathrm{II}}(x)$:

$$\Psi_{\mathrm{II}}(x) = Ce^{\beta x} + De^{-\beta x} \quad \text{with}\,;\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$
$$\Psi_{\mathrm{II}}(x) = e^{ikx}\left(Ce^{(\beta-ik)x} + D^{-(\beta+ik)x}\right)$$

To ensure a continuous function, we require

$$\Psi_{\mathrm{I}}(0) = \Psi_{\mathrm{II}}(0)\,, \quad \left.\frac{\mathrm{d}\Psi_{\mathrm{I}}}{\mathrm{d}x}\right|_{x=0} = \left.\frac{\mathrm{d}\Psi_{\mathrm{II}}}{\mathrm{d}x}\right|_{x=0}$$

From Bloch's theorem, $u(x)$ must be periodic:

$$u_{\mathrm{I}}(a-b) = u_{\mathrm{II}}(-b)\,, \quad \left.\frac{\mathrm{d}u_{\mathrm{I}}}{\mathrm{d}x}\right|_{x=a-b} = \left.\frac{\mathrm{d}u_{\mathrm{II}}}{\mathrm{d}x}\right|_{x=-b}$$

These four conditions give the equation

$$\cos(ka) = \cos(\alpha(a-b))\cosh(\beta b) + \frac{\beta^2 - \alpha^2}{2\alpha\beta}\sin(\alpha(a-b))\sinh(\beta b)\,. \tag{4.13}$$

This equation gives the permitted energies of the system, as some energy values will result in the LHS being > 1 and therefore having no corresponding k value.

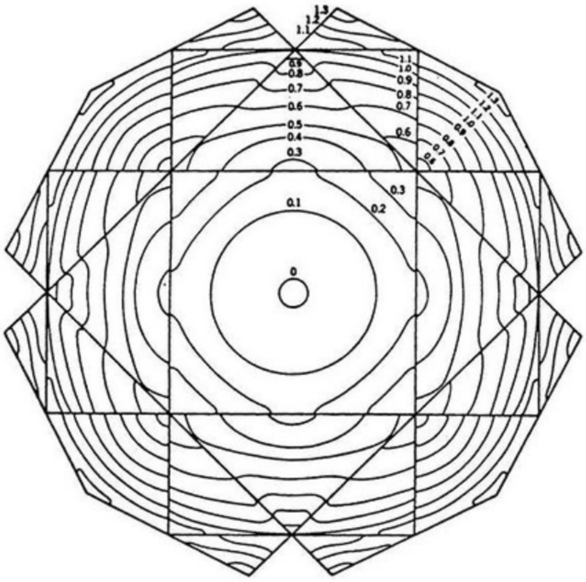


Figure 14: Energy contours (in eV) of a hypothetical square lattice. The first four Brillouin zones are shown by the straight lines. Note the perfect circles near the centre (as would be expected from the free electron model) but there are discontinuities at Brillouin zone boundaries.

The nearly free electron model gives rise to an energy gap Δ between the bound valence electrons and the free electrons that are able to conduct heat and electricity. If the Fermi level lies below the conduction band, that material is an insulator. Electrons are unable to be excited into the conduction band and the material cannot conduct electricity. There will also be no electronic contribution to the specific heat for $k_{\mathrm{B}}T < \Delta$. Light with $\hbar\omega < \Delta$ will not be able to be absorbed meaning insulators are transparent to light in this region. If $\Delta \lesssim 2\,\mathrm{eV}$, the material is called a semiconductor.

4.4 Semiconductors

Group IV elements (C, Si, Ge) have four loosely bound valence electrons. At finite temperature T, some of these will be excited to the conduction band, allowing the material to conduct a small amount. However, the pure elements do not conduct enough to be useful. Very small amounts of impurities (order of one part in 10^5) can make a huge difference to their conductivities. This is called *doping*. A semiconducting material can be doped in two ways: n-type is where a group V element (e.g. As) is added as this has one additional electron per atom; p-type is where a group III element (e.g. Ga) is added as this has one fewer electron per atom. The “p” and “n” stand for “positive” and “negative” and refer to the charge of the majority charge carriers rather than the overall charge of the material, which remains neutral. The impurities introduce additional energy states which are shown in figure 15.a. A p-type semiconductor has additional states just above the valence band meaning an electron can easily be excited to it, leaving a *hole* in the valence band. These positive holes are the charge carriers. An n-type semiconductor has additional states just below the conduction band meaning electrons can easily excite to the conduction band and become the charge carriers.

The chemical potential μ (also called the Fermi level) is equal to the Fermi energy at $T = 0$. It is the energy required to add another electron to the system and can be though of as a hypothetical energy level which would have a 50% chance of being occupied if it existed. In an n-type semiconductor, this lies just above the occupied donor states and in a p-type semiconductor it lies just below the unoccupied acceptor states.

A p-n junction occurs at the boundary between a p-type and an n-type semiconductor. There will be an initial flux of particles across the interface where electrons and holes recombine. When equilibrium is reached, both regions will have the same chemical potential. This is shown in figure 15.b. There, materials are no longer electrically neutral so there is now an electric field $\boldsymbol{\epsilon}$ across the boundary.

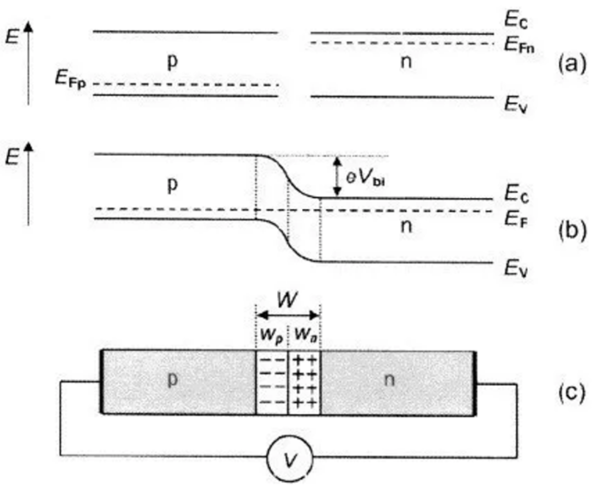


Figure 15: (a) A p-type and an n-type semiconductor with the chemical potentials shown, such that $E_{\mathrm{F}_p} - E_V \simeq E_C - E_{\mathrm{F}_n} \ll \Delta = E_C - E_V$. (b) The two semiconductors are joined together, forming a p-n junction. (c) A p-n junction with a voltage applied across it; the depletion region where electrons and holes have recombined is shown.

In equilibrium there are four currents across the junction. There are recombination currents of holes i_{pr} and electrons i_{nr}. Electron-hole pairs can be generated by thermal excitations across the band gap resulting in minority charge carriers. The $\boldsymbol{\epsilon}$ field will sweep these out of the junction leading to thermal generation currents i_{pg}, $i_{ng} \propto e^{-\Delta/k_{\mathrm{B}}T}$. These currents will be balanced at equilibrium:

$$i_{pr} + i_{pg} = 0, \quad i_{nr} + i_{ng} = 0$$

The recombination currents will also be proportional to $e^{-\Delta/k_{\mathrm{B}}T}$ as the potential barrier they need to overcome is $\approx \Delta$.

A forward bias voltage V_{appl} can be applied across the p-n junction. This will oppose $\boldsymbol{\epsilon}$ and decrease the difference between the energy levels by $\Delta E = -eV_{\mathrm{appl}}$. It therefore becomes easier for the recombination currents to overcome the potential barrier. These are increased by a factor $\exp\left(\frac{eV_{\mathrm{appl}}}{k_{\mathrm{B}}T}\right)$ but the thermal generation currents remain unaffected Thus, the net currents are

$$\begin{aligned} i_p = i_{pr} + i_{pg} = |i_{pg}| \left(\exp\left(\frac{eV_{\mathrm{appl}}}{k_{\mathrm{B}}T}\right) - 1\right) \\ i_n = i_{nr} + i_{ng} = |i_{ng}| \left(\exp\left(\frac{eV_{\mathrm{appl}}}{k_{\mathrm{B}}T}\right) - 1\right) \end{aligned}$$

Which gives a total current of

$$I = i_s \left(\exp\left(\frac{eV_{\mathrm{appl}}}{k_{\mathrm{B}}T}\right) - 1\right) , \tag{4.14}$$

where $i_s = |i_{pg}| + |i_{ng}|$ is called the saturation current. This means the p-n junction will only allow current to flow in one direction. These can be used as simple diodes, but also form the basis for more complex circuit components such as transistors and photovoltaic cells.

5 Nuclear & Particle Physics

5.1 Nuclear Matter

So far, nuclei have been treated as static point charges which just set up a potential for electrons. However, we can zoom in to length scales of femtometres to look at the structure of nuclei themselves. Scattering experiments show that nuclei can be roughly modelled as spheres with a radius R dependent on the total number of nucleons A

$$R = R_0 A^{\frac{1}{3}}\,, \tag{5.1}$$

where $R_0 \approx 1.2$ fm; hence, the volume is proportional to A. Masses of nuclei are measured in unified atomic mass units u such that $M \approx Au$ is the mass of the nucleus. The value of u is defined as one twelfth the mass of a $^{12}_{6}\mathrm{C}$ atom such that $u = 1.6605\ldots \times 10^{-27}$ kg is roughly the mass of either a proton or neutron. Nuclear masses will be slightly lower than the sum of the constituent nucleons due to the binding energy holding them together. Also, because both the volumes and masses of nuclei are almost proportional to A, all nuclei have approximately the same density: $\rho \approx 2.3 \times 10^{17}\ \mathrm{kg\,m^{-3}}$.

The energy required to separate a nucleus into separate protons and neutrons is the binding energy E_B

$$E_\mathrm{B} = (Zm_\mathrm{p} + Nm_\mathrm{n})c^2 - Mc^2\,, \tag{5.2}$$

for a nucleus with Z protons and N neutrons. The most stable nuclei have a binding energy of around 9 MeV per nucleon.

The strong nuclear force overcomes the electrostatic repulsion of the protons to hold the nucleus together. It must have the following characteristics:

- Independent of electric charge
- Very short-ranged (10^{-15} m)
- Results in a constant density and similar binding energies per nucleon

This suggests that each nucleon interacts only with nucleons in its immediate vicinity and these interactions are saturated (like covalent bonding in molecules). Also, the nuclear force favours pairs of protons or neutrons due to spin-spin coupling, e.g. $^{4}_{2}\mathrm{He}$ is particularly stable.

The Liquid Drop Model

Based on these observations, several similarities between nuclei and liquid drops were noticed. An empirical model which treated nuclei as drops of an incompressible fluid was proposed by George Gamow and developed by Niels Bohr and John Archibald Wheeler. This gives an equation for the binding energy with five terms:

1. Volume energy $\propto A$: Since the nuclear force always shows saturation, each interior nucleon interacts with the same number of other nucleons. So this energy is proportional to volume.
2. Surface energy $\propto -A^{2/3}$: Nucleons on the surface will not interact with this number of other nucleons so a correction term proportional to the surface area needs to be added.
3. Coulomb energy $\propto -\frac{Z(Z-1)}{A^{1/3}}$: There is a repulsive Coulomb force between each pair of protons.
4. Asymmetry/Pauli energy $\propto -\frac{(N-Z)^2}{A}$: There are unequal numbers of protons and neutrons for heavier nuclides implying higher energy levels are filled for neutrons than protons.
5. Pairing energy $\propto \pm\frac{1}{A^{4/3}}$: To account for the tendency of proton pairs and neutron pairs to occur, this term is positive if both Z and N are even, negative if they are both odd, and zero if one is odd and the other is even.

So the total equation is

$$E_\mathrm{B} = c_1 A - c_2 A^{2/3} - c_3 \frac{Z(Z-1)}{A^{1/3}} - c_4 \frac{(N-Z)^2}{A} \pm c_5 \frac{1}{A^{4/3}}\,, \tag{5.3}$$

where c_{1-5} are experimentally determined constants. This model gives a good approximation for nuclear masses but fails to explain lines of greater binding energy at certain numbers of protons and neutrons.

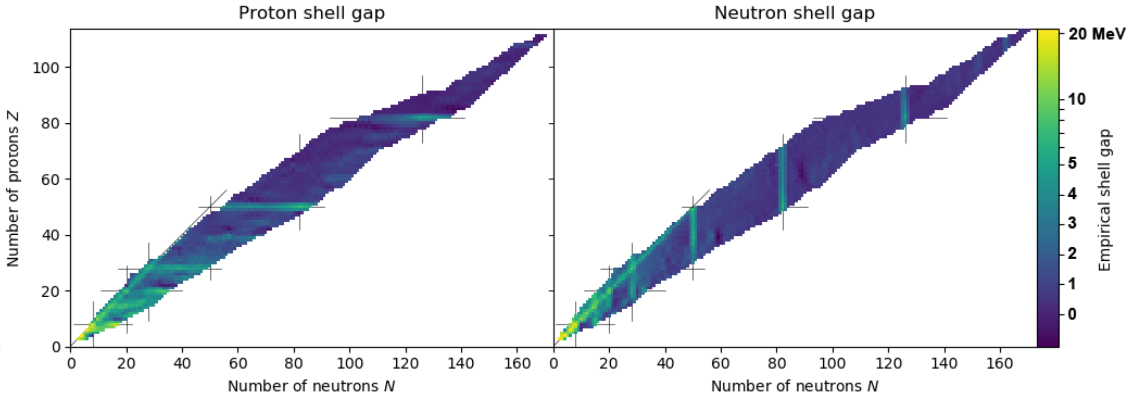


Figure 16: The empirical proton and neutron shell gaps, obtained from observed binding energies. Distinct shell gaps appear at the magic numbers, and at $N = Z$.

The Nuclear Shell Model

We can consider each nucleon to be moving in a potential set up by the rest of the nucleus - neutrons in a potential set up by the nuclear force, protons in a potential which also includes the Coulomb force. We can solve the Schrödinger equation for each of these potentials and, because these potentials are spherically symmetric, angular momentum is conserved. This gives a shell structure to energy states analogous to the atomic shell model of electrons. There are therefore a set of nucleon numbers which produce very stable nuclei; these are called the *magic numbers*:

$$2,\ 8,\ 20,\ 28,\ 50,\ 82,\ 126$$

Note, the shells for protons and neutrons are independent of each other. So, magic nuclei occur when one of the nucleon type equals a magic number, and *doubly magic nuclei* occur when both do.

How Heavy can a Nucleus be?

Among the over 2500 known nuclides, only about 300 are stable. The others undergo decays including β^- decay (neutron-rich nuclides), β^+ decay (proton-rich nuclides), and α decay (heavier nuclides):

$$\begin{aligned} {}^{60}\mathrm{Co} &\longrightarrow {}^{60}\mathrm{Ni} + \beta^- + \bar{\nu} \\ {}^{64}\mathrm{Cu} &\longrightarrow {}^{64}\mathrm{Ni} + \beta^+ + \nu \\ {}^{228}\mathrm{Th} &\longrightarrow {}^{224}\mathrm{Ra} + {}^{4}\alpha \end{aligned}$$

For an electron “orbiting” a nucleus, we can equate the centripetal and Coulomb forces and use the fact that $mvr = n\hbar$ is the quantised angular momentum to get

$$v = \frac{Ze^2}{4\pi\varepsilon_0\hbar},$$

as the velocity of a ground-state electron. However, this is limited by the speed of light, giving

$$Z_{\mathrm{max}} = \frac{4\pi\varepsilon_0\hbar c}{e^2} = \alpha^{-1}, \tag{5.4}$$

where $\alpha \approx \frac{1}{137}$ is the *fine structure constant*. This means that $Z_{\mathrm{max}} \approx 137$. The heaviest nuclide found so far is an isotope of Oganesson ${}^{294}_{118}\mathrm{Og}$.

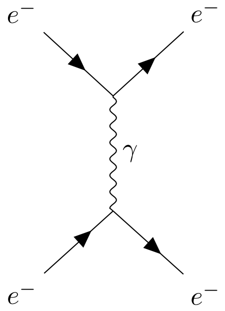
5.2 The Standard Model

The Standard Model of particle physics is a theory developed in the mid 20th century which categorises the elementary particles and explains interactions between them through three fundamental forces. There are four types of fermion: up quark, down quark, electron, and neutrino, and there are three *generations* of each of these. These are the particles which make up matter and all have $s = \frac{1}{2}$. The interactions between these are described by quantum field theory (QFT) and correspond to the exchange of $s = 1$ force-carrying quanta called gauge bosons:

- Electromagnetic: described by quantum electrodynamics (QED) and the exchange of photons
- Strong: described by quantum chromodynamics (QCD) and the exchange of gluons (on the length scale of quarks) or mesons (on the length scale of nucleons)
- Weak: can either be a charged-current interaction (with the exchange of W bosons) or a neutral-current interaction (with the exchange of Z bosons)

The final boson in the Standard Model is the Higgs boson which was discovered in 2012. This has $s = 0$ and provides a mechanism by which other particles acquire mass.

Feynman diagrams can be used to describe some amplitude for a process. This is written in powers of an expansion parameter g which describes how strongly a particle couples to a field and related to the probability of a process occurring. An example Feynman diagram for an $e^- - e^-$ interaction is shown:



A quantity $\alpha_{\text{EM}} \propto g^2$ measures the strength of the coupling, i.e. the amplitude of an electron emitting and absorbing a photon as shown in the diagram. The virtual photon is created from *borrowed energy* due to the uncertainty principle $\Delta E \Delta t \sim \hbar$. For a particle separation r, the energy change is

$$\Delta E \sim \frac{\hbar}{\Delta t} = \frac{\hbar c}{r},$$

and the strength of the coupling is

$$\alpha_{\text{EM}} = \frac{e^2}{4\pi\varepsilon_0 r}(\Delta E)^{-1} = \frac{e^2}{4\pi\varepsilon_0 r}\frac{r}{\hbar c} = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137}$$

which is the fine structure constant. Similar analysis can be done for the other interactions to get

$$\alpha_{\text{S}} \approx 1\,; \quad \alpha_{\text{W}} \approx \frac{1}{30}\,.$$

This means that the three interactions have relative strengths $1 : \frac{1}{30} : \frac{1}{137}$.

5.2.1 Klein-Gordon Equation

There is one major problem with using quantum mechanics to describe elementary particles: the Schrödinger equation does not take into account special relativity, but elementary particles often move at relativistic speeds. We require a wave equation with solutions satisfying $E^2 = p^2c^2 + m^2c^4$. From the correspondence principle, we know that $\hat{E} = i\hbar\frac{\partial}{\partial t}$ and $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$ for a plane wave (free particle) solution. These can be substituted into the relativistic energy equation to get the Klein-Gordon equation.

$$-\hbar^2\frac{\partial^2\Psi}{\partial t^2} = \left(-\hbar^2c^2\nabla^2 + m^2c^4\right)\Psi\,. \tag{5.5}$$

However, one of the solutions to the new dispersion relation $E = \pm\sqrt{p^2c^2 + m^2c^4}$ is negative. If we compare the Klein-Gordon equation to the continuity equation (like in section 4.2), we find that the probability density is proportional to the energy, meaning the negative energy solution is unphysical.

5.2.2 Dirac Equation

To overcome this problem, Dirac proposed an alternative wave equation. Special relativity implies that space and time should be treated equally, so we want an equation which contains both first order space and time derivatives. If we let the Hamiltonian be

$$\hat{H} = \alpha_x c\hat{p}_x + \alpha_y c\hat{p}_y + \alpha_z c\hat{p}_z + \beta mc^2 \,, \tag{5.6}$$

then we can select α, β values such that $\hat{H}^2\Psi = -\hbar^2 \frac{\partial^2\Psi}{\partial t^2}$ becomes equation 5.5. Substituting the momentum operators in, this becomes

$$\begin{aligned}\hat{H}^2\Psi = &- \hbar^2c^2 \left(\alpha_x\frac{\partial}{\partial x} + \alpha_y\frac{\partial}{\partial y} + \alpha_z\frac{\partial}{\partial z}\right)\left(\alpha_x\frac{\partial}{\partial x} + \alpha_y\frac{\partial}{\partial y} + \alpha_z\frac{\partial}{\partial z}\right)\Psi \\ &- i\hbar mc^3 \left(\alpha_x\beta\frac{\partial}{\partial x} + \alpha_y\beta\frac{\partial}{\partial y} + \alpha_z\beta\frac{\partial}{\partial z}\right)\Psi \\ &- i\hbar mc^3 \left(\beta\alpha_x\frac{\partial}{\partial x} + \beta\alpha_y\frac{\partial}{\partial y} + \beta\alpha_z\frac{\partial}{\partial z}\right)\Psi \\ &+ \beta^2m^2c^4\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial t^2}\end{aligned}$$

If we let $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1$, we require each of the cross-terms to cancel out, i.e. $\alpha_x\alpha_y = -\alpha_y\alpha_x$, $\alpha_x\beta = -\beta\alpha_x$, and so on. We therefore require $\alpha_x, \alpha_y, \alpha_z, \beta$ to be 4×4 matrices. Solutions are not unique but the most conventional set of matrices are called the gamma matrices

$$\begin{aligned}\beta = \gamma^0 &= \begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\end{pmatrix} = \begin{pmatrix}\boldsymbol{I} & \mathbf{0}\\ \mathbf{0} & -\boldsymbol{I}\end{pmatrix}\\ \alpha_x = \gamma^1 &= \begin{pmatrix}0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\\ 0 & -1 & 0 & 0\\ -1 & 0 & 0 & 0\end{pmatrix} = \begin{pmatrix}\mathbf{0} & \sigma_x\\ -\sigma_x & \mathbf{0}\end{pmatrix}\\ \alpha_y = \gamma^2 &= \begin{pmatrix}0 & 0 & 0 & -i\\ 0 & 0 & i & 0\\ 0 & i & 0 & 0\\ -i & 0 & 0 & 0\end{pmatrix} = \begin{pmatrix}\mathbf{0} & \sigma_y\\ -\sigma_y & \mathbf{0}\end{pmatrix}\\ \alpha_z = \gamma^3 &= \begin{pmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\\ -1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{pmatrix} = \begin{pmatrix}\mathbf{0} & \sigma_z\\ -\sigma_z & \mathbf{0}\end{pmatrix}\end{aligned} \tag{5.7}$$

which can be written as block matrices in terms of the Pauli spin matrices, where $\boldsymbol{I}$ and $\mathbf{0}$ are the 2×2 identity and zero matrices, respectively. Using our new Hamiltonian in the TDSE:

$$\left[-i\hbar c\left(\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\right) + \beta mc^2\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t} \,. \tag{5.8}$$

This is the Dirac equation for a free particle. $\Psi(\mathbf{r}, t)$ must have four components, each a function of both position and time.

To solve this equation, we can propose a solution of the form

$$\Psi(x,y,z,t) = \begin{pmatrix} u_1(p) \\ u_2(p) \\ u_3(p) \\ u_4(p) \end{pmatrix} e^{i(pz-Et)/\hbar}$$

for momentum p. This is a free particle solution to the Schrödinger equation (with no x or y dependence) multiplied by the Dirac spinor. Therefore, we get

$$\left(-i\hbar c\alpha_z \frac{\partial}{\partial z} + \beta mc^2\right)\Psi(z,t) = i\hbar\frac{\partial \Psi}{\partial t}$$

$$-i\hbar c\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}\frac{ip}{\hbar}\Psi(z,t) + \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} mc^2\Psi(z,t) = E\Psi(z,t)$$

$$pc\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} u_1(p) \\ u_2(p) \\ u_3(p) \\ u_4(p) \end{pmatrix} + mc^2\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} u_1(p) \\ u_2(p) \\ u_3(p) \\ u_4(p) \end{pmatrix} = E\begin{pmatrix} u_1(p) \\ u_2(p) \\ u_3(p) \\ u_4(p) \end{pmatrix}$$

This gives

$$\begin{pmatrix} E-mc^2 & 0 & -pc & 0 \\ 0 & E-mc^2 & 0 & pc \\ pc & 0 & E+mc^2 & 0 \\ 0 & -pc & 0 & E+mc^2 \end{pmatrix}\begin{pmatrix} u_1(p) \\ u_2(p) \\ u_3(p) \\ u_4(p) \end{pmatrix} = 0$$

This set of four coupled equations will give non-trivial solutions of E when the determinant of the matrix is zero. Setting the determinant equal to zero gives

$$\begin{aligned} (E-mc^2)(E+mc^2(E^2-m^2c^4-p^2c^2)) - pc(pc(E^2-m^2c^4-p^2c^2)) &= 0 \\ (E^2-m^2c^4-p^2c^2)^2 &= 0 \\ \Rightarrow E^2-m^2c^4-p^2c^2 &= 0 \qquad (5.9) \end{aligned}$$

Which returns the result from special relativity. For the positive energy solution $E = +\sqrt{p^2c^2+m^2c^4}$, we get

$$u_3(p) = \frac{-cpu_1(p)}{E+mc^2}\,, \quad u_4(p) = \frac{cpu_2(p)}{E+mc^2}$$

The other two equations from the matrix equation are not valid for the positive energy solution in the rest frame of the particle, i.e. $p = 0$. This gives wavefunctions of

$$\Psi_\uparrow(z,t) = \begin{pmatrix} 1 \\ 0 \\ \frac{-cp}{E+mc^2} \\ 0 \end{pmatrix} e^{i(pz-Et)/\hbar}\,, \quad \Psi_\downarrow(z,t) = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \frac{cp}{E+mc^2} \end{pmatrix} e^{i(pz-Et)/\hbar}$$

The total solution Ψ is then a linear superposition of these.

Similarly for the negative energy solution $E = -\sqrt{p^2c^2+m^2c^4}$, Ψ will be a linear superposition of

$$\Psi_\uparrow(z,t) = \begin{pmatrix} \frac{cp}{E-mc^2} \\ 0 \\ 1 \\ 0 \end{pmatrix} e^{i(pz-Et)/\hbar}, \quad \Psi_\downarrow(z,t) = \begin{pmatrix} 0 \\ \frac{-cp}{E-mc^2} \\ 0 \\ 1 \end{pmatrix} e^{i(pz-Et)/\hbar}$$

Unlike with the Klein-Gordon equation, when compared with the continuity equation, we find that the probability density is positive for all energies. The negative energy solutions led to the theory of antiparticles. Dirac proposed that all negative energy states are filled and the Pauli exclusion principle prevents particles from falling into these states. However, negative energy particles can be excited into a positive state by a photon, leaving a hole (the antiparticle) in the vacuum. This is pair production. Similarly, annihilation occurs when the particle drops back into the negative state, annihilating the hole and producing photons. This model is useful to conceptualise antimatter but has since been superseded by QFT - an infinite number of antiparticles poses a significant problem if they are to have mass as this model suggests.

In the non-relativistic limit $c^2 \to \infty$ we can see that $\Psi_{3,4} \to 0$ for the case of the positive energy solution. This means that the free particle solution becomes that of the Schrödinger equation multiplied by the $\chi_\pm$ spinors from equation 3.16. It can therefore be seen that spin naturally arises from the Dirac equation.